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A DICTIONARY

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AND THE

ALLIED BRANCHES OF OTHER SCIENCES.

BY

HENRY WATTS, B.A., F.C.S.

EDITOR OF

'THE JOURNAL OF THE CHEMICAL SOCIETY.'

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IN FIVE VOLUMES.

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⁂ Articles communicated by the several contributors are signed with their initals; articles taken from URE's *Dictionary of Chemistry* (fourth edition, 1831) are signed with the letter U; those which have no signature are by the Editor.

DICTIONARY OF CHEMISTRY.

H.

HÆMAPHEIN. *Blood-brown.* (Simon, *Medicin. Chem.* i. 328; Handw. d. Chem. 2^{te}. Aufl. ii. [2] 157.) A brown substance, probably a product of the decomposition of hæmatin, obtained from blood by the following process:—Dried blood is repeatedly exhausted with boiling water, warm ether, and lastly with alcohol containing sulphuric acid, and the latter solution, after supersaturation with ammonia, is evaporated to dryness. The residue is exhausted with alcoholic ammonia, the solution is again evaporated to dryness, and the residue is exhausted with ether, and then repeatedly with water, in which the hæmaphein dissolves. To free it from still admixed hæmatin, it is dried, dissolved in boiling alcohol, separated again by evaporation, then dissolved in cold alcohol, and the alcohol is evaporated. The product thus obtained is a brown mass difficult to pulverise, soluble with brown-red colour in cold alcohol, less soluble in water and in ether. It does not melt when heated, but burns with a bright flame, without leaving any ash. The solution in dilute alcohol forms brown precipitates with lead, copper, mercurous and silver salts. Sanson obtained a body of similar colour to the above by treating blood successively with alcohol and water.

HÆMATEIN. $C^{16}H^{12}O^6$, or $C^{16}H^{10}O^5$. (Erdmann, Ann. Ch. Pharm. xliv. 294.—Hesse, *ibid.* cix. 232.)—A substance produced from hæmatoxylin by abstraction of 2 at. hydrogen, a change which takes place by the action of oxygen under the influence of alkalis. The best mode of preparing it is to sprinkle about 20 grms. of hæmatoxylin in a basin with sufficient ammonia to dissolve it, stirring continually, and warming the liquid gently as long as the hæmatoxylin remains in excess. It must now be exposed to the air, and ammonia added from time to time by small quantities, so that the liquid may always smell of it, care being however taken not to add too much ammonia, as it would cause decomposition. The liquid after a little while assumes a dark red colour, appearing almost black when viewed in a stratum of moderate depth. It then contains hæmateate of ammonium, and on being slightly supersaturated with acetic acid, deposits hæmatein in the form of a bulky brown-red mass, like ferric hydrate, which by drying acquires a deep green colour and metallic lustre: its powder in thin layers, exhibits a red colour.

Hæmatein dissolves slowly in cold, more readily in boiling water. On quickly evaporating a solution prepared at the boiling heat, it becomes covered with shining green scales, which sink to the bottom and are gradually replaced by others. Sometimes also the solution solidifies in a gelatinous mass, which yields micaceous laminæ when suspended in water. Hæmatein likewise dissolves in alcohol and very sparingly in ether. It dissolves with red-brown colour in the mineral acids, less easily in acetic acid. Sulphydric acid decolorises it, but does not convert it into hæmatoxylin. It is carbonised by heat.

Hæmatein unites readily with bases. *Potash* dissolves it, forming a blue solution, which turns brown on exposure to the air. *Ammonia* dissolves it with a fine purple colour, which likewise turns brown in the air.

The last-mentioned solution contains **hæmateate of ammonium**, which is likewise formed when a solution of hæmatoxylin in ammonia is exposed to the air. The salt deposited by gradual evaporation is a dark violet, granular powder, which, when examined by the microscope, appears to be composed of transparent, violet, four-sided prisms. It contains, according to Erdmann's analysis, 56·26 per cent. C, 5·17 H, and 6 72 N (mean), whence Gerhardt (*Traité*, iv. 303) deduced the formula $C^{16}H^{10}(NH^4)^2O^6$ (57·5 C, 5·4 H, and 8·3 N). Hesse, by leaving the solution to stand for two or three days in a cool place, obtained crystals in which he found 51·87 C, 5·78 H, and 3·55 N (mean), agreeing nearly with the formula $C^{16}H^9(NH^4)O^5.4H^2O$, which requires 51·75 C, 5·66 H, and 3·77 N. Hæmateate of ammonium dissolves readily in water and alcohol. The alcoholic solution is red-brown, but becomes purple on addition of water. The salt gives off water and ammonia at 100° C. and must therefore be dried over sulphuric acid at ordinary temperatures; even then it sometimes decomposes. Over sulphuric acid in vacuo, it gives off all its ammonia and leaves hæmatein (Erdmann). According to Hesse, it gives off all its water and ammonia at 130° C., leaving hæmatein as a very hygroscopic powder, having a blackish violet colour with green iridescence.

Hæmatein thus obtained contains, according to Hesse's analysis, 67·66 per cent. carbon, and 3·50 hydrogen, agreeing nearly with the formula $C^{16}H^{10}O^5$, which requires 68·08 C and 3·54 H. Erdmann found in his hæmatein 62·66 per cent. C and 4·16 H (mean), whence he deduced the formula $C^{40}H^{32}O^{16}$. Gerhardt (*Traité*, iv. 302) proposed the formula $C^{16}H^{12}O^6$, which, however, does not agree very well with Erdmann's analyses, requiring 64·0 per cent. C and 4·0 H. Hesse suggests that Erdmann's hæmatein may be a dibasic acid, $\left.\begin{matrix}C^{16}H^{10}O^4\\H^2\end{matrix}\right\}O^2$, and the product, $C^{16}H^{10}O^5$, obtained by himself, the corresponding anhydride; on this supposition, the two ammonium-salts above mentioned are, perhaps, $\left.\begin{matrix}C^{16}H^{10}O^4\\(NH^4)^2\end{matrix}\right\}O^2$ and $\left.\begin{matrix}C^{16}H^{10}O^4\\H.NH^4\end{matrix}\right\}O^2.3H^2O$.

The solution of hæmateate of ammonium forms coloured precipitates with many metallic salts: with acetate of *lead* it produces a deep blue precipitate; with sulphate of *copper*, violet-blue; with *protochloride of tin*, violet; with *iron-alum*, black. With chloride of *barium* it forms a dark purple liquid, which becomes brown on exposure to the air. It reduces nitrate of *silver*, but has no action on mercuric chloride. According to Hesse, it forms with *chloride of barium*, *chloride of calcium*, and especially with *chloride of sodium*, precipitates of various colours; no precipitate with hyposulphite of sodium; with *acid sulphite of ammonium*, a gelatinous precipitate, which disappears on boiling.

HÆMATIN or HÆMATOSIN. The red colouring matter of the blood-corpuscles. (See BLOOD, i. 607.) Lehmann (Compt. rend. xl. 385) first showed that it may be obtained in the crystalline state. R. Schwarz (Zeitschr. f. die ges. Naturwissench. xi. 225) prepares it in this state by submitting the comminuted clot of ox-blood, freed as much as possible from serum, to pressure, and agitating the expressed liquid by small portions with a saturated solution of oxalic acid, with addition of alcohol and a large quantity of ether. The clear dark brown solution, decanted after a few minutes and left to stand for some weeks over chloride of calcium, deposits the hæmatin in small black nodules made up of cubes, which may be freed from admixed oxalate of calcium by means of dilute hydrochloric acid. Less distinct crystals may be obtained by leaving the ethereal solution to evaporate freely; but the quantity is always small. A solution of hæmatin obtained as above from horse-blood, yielded, on standing, small rush-shaped or spindle-shaped crystals, red-brown by transmitted light. Hæmatin may be obtained in the amorphous state by distilling off about a third of the ether from the solution, and mixing the residue with a large quantity of water. The black flocks thus precipitated are washed with water by decantation; then boiled with strong acetic acid, to free them from albuminous compounds, as long as the liquid is rendered turbid by ferrocyanide of potassium; and, lastly, the precipitate is boiled with water, alcohol, and ether in succession, and then again treated with water. The crystallised compound may be subjected to the same treatment without undergoing any alteration. Hæmatin thus prepared is tasteless and inodorous, insoluble in water, cold alcohol, and ether; partially (?) soluble in hot alcohol, easily in acidulated alcohol, whence it is precipitated by water. The solution in acidulated alcohol is decolorised by peroxide of lead. Hæmatin likewise dissolves easily in slightly alkaline liquids, but not in strong sulphuric or hydrochloric acid. Silver, lead, and copper-salts form precipitates in the ammoniacal solution. Hæmatin, when burnt, leaves a residue of ferric oxide mixed with small quantities of calcic phosphate.

The following analyses of hæmatin by Schwarz, give results not differing greatly from those formerly obtained by Mulder (whence the latter deduced the formula $C^{22}H^{22}FeN^3O^3$), but agreeing better with the formula $C^{43}H^{42}FeN^3O^2$.

	Calculation.	Schwarz.			Mulder.
		Amorphous.		Crystallised from horse-blood.	
C^{23}	66·35	64·12	63·89	64·03	65·55
H^{22}	5·28	5·31	5·28	5·60	5·30
Fe	6·73	6·36	. .	. .	6·73
N^3	10·10	10·19	. .	10·17	10·54
O^3	11·54	11·00	. .	. .	11·85
Phosphate of calcium	. .	3·02			
	100·00	100·00			100·00

When an alcoholic solution of crystallised hæmatin is boiled with nitric acid, the whole of the nitrogen of the hæmatin is removed, and a non-azotised acid is formed, together with a substance which reduces cupric oxide in alkaline solution, and ferments with yeast, yielding alcohol and carbonic acid.

The name *hæmatin* is sometimes also used as a synonyme of HÆMATOXYLIN.

HÆMATINONE. A red glass known to the ancients, and used for mosaics, ornamental vases, &c.; it is mentioned by Pliny, and occurs pretty frequently among the ruins of Pompeii. Its colour is a fine red, intermediate between red lead and vermilion. It is opaque, harder than common glass, takes a fine polish, has a conchoïdal fracture, and a specific gravity of 3·5. The red colour, which is due to red oxide of copper, is completely destroyed by fusion, and cannot be restored by any addition whatever. The fused mass has a greenish black colour, which reducing agents merely convert into a muddy brown-red. Hæmatinone contains no tin, and no colouring substance except cuprous oxide.

This antique glass may be exactly imitated by the following process, discovered by Pettenkofer (Dingl. pol. J. cxlv. 122):—100 pts. of silica, 11 lime, 1 magnesia, 33 litharge, and 50 carbonate of soda, are fused together, and to the clear white glass thus produced are added 25 pts. of scale oxide of copper, somewhat later 2 pts. of scale oxide of iron, and, lastly, a small quantity of charcoal. On leaving the fused mass to cool slowly, a liver-coloured glass is obtained, which, when further heated (for 6 to 12 hours) till it softens, is converted into hæmatinone of a splendid red colour, in consequence of the separation of a red cuprous compound within its mass.

A more fusible glass, made by melting together 100 pts. silica, 10 lime, 0·5 magnesia, 40 litharge, 60 carbonate of soda, 30 scale oxide of copper, 2 alumina, and 3 scale oxide of iron, exhibits, after once slow cooling in the air-furnace, a great number of red points, diffused through a yellowish vitreous mass; on cutting and polishing this glass, the red points appear as beautiful tufts of needle-shaped crystals.

When part of the silica in hæmatinone is replaced by boric anhydride (by adding borax to the melted mass), a dark-coloured, dichroïtic, crystalline compound is obtained, called astralite (i. 429).

Pettenkofer is of opinion that the same crystalline cuprous compound (whether pure cuprous oxide, or more probably cuprous silicate) which imparts the red colour to hæmatinone, constitutes likewise the crystalline spangles contained in aventurin glass (i. 477), which in fact he has produced by fusing hæmatinone with a quantity of iron filings, sufficient to reduce about half the copper contained in it to the metallic state (the metal then settling down in the form of a regulus, and leaving a deep greenish black, scarcely transparent glass above), heating this glass for some time to the temperature at which it softens, and then leaving it to cool very slowly. (Jahresb. d. Chem. i. 1061; ix. 798.)

HÆMATITE. Native sesquioxide of iron. (See IRON, OXIDES OF.)

HÆMATO-CRYSTALLIN. A crystalline substance obtained from blood (i. 606). It has the composition of the albuminoïds, and if quite pure would probably be colourless, but it has never yet been obtained perfectly free from hæmatin.

HÆMATO-GLOBULIN. Syn. with HÆMATO-CRYSTALLIN.

HÆMATOÏDIN. A crystalline substance often found in extravasated blood (i. 607). It appears to be produced by the decomposition of hæmatin; but the nature of the transformation has not been exactly made out. According to Verdeil and Dollfus (Compt. rend. xxx. 306), crystals resembling hæmatoïdin may be obtained from ox-blood by filtering it after coagulation by heat; evaporating the solution to a syrup, and mixing it with alcohol; strongly concentrating the liquid filtered from the resulting precipitate; and mixing it, when cold, with dilute sulphuric acid. Fat globules then separate on the surface of the liquid, and sometimes red crystals resembling hæmatoïdin.

Robin (Compt. rend. xli. 506) found a considerable quantity of hæmatoïdin in an hepatic cyst, forming hard, brittle prisms of 118° and 62°, and of a bright, orange-red colour. According to Valentiner (Jahresb. d. Chem. 1859, p. 656), gall-stones, bile, and the livers of persons affected with jaundice, yield, when treated with chloroform, a crystalline substance differing from all previously known ingredients of bile, and agreeing in all respects with hæmatoïdin.

HÆMATOSIN. See Hæmatin.

HÆMATOXYLIN, also called *Hematin.* $C^{16}H^{14}O^{6}$. (Chevreul, Ann. Chim. lxxx. 128.—Golfier-Besseyre, Ann. Ch. Phys. [2] lxx. 272.—Erdmann, Ann. Ch. Pharm. xliv. 292.—Leblanc, *Traité de Chimie* de Dumas, viii. 102.—O. Hesse, J. pr. Chem. lxxv. 218; Ann. Ch. Pharm. cix. 332.)—A crystalline substance contained in logwood (*Hæmatoxylon Campechianum*), and the source of the colouring properties of that well-known dye. In the pure state, however, it has little or no colour, but is converted into a colouring matter under the influence of alkalis and oxygen.

It is prepared by leaving the commercial extract of logwood—previously mixed with quartz-sand to prevent agglomeration—in contact with 5 or 6 times its volume of ether (not anhydrous) for several days, agitating from time to time; then decanting the brownish-yellow solution; distilling off the ether; mixing the syrupy residue with water; and leaving it to itself in a loosely covered vessel. If no water were added, the liquid would simply dry up to a gummy mass; but, if a sufficient quantity of water is present, the hæmatoxylin crystallises in the course of a few days. The crystals are washed with water and freed from adhering mother-liquor by pressure between filtering paper. The mother-liquor mixed with the wash-water yields another crop of crystals by spontaneous evaporation. A kilogramme of logwood treated several times with ether yields from 100 to 120 grms. of hæmatoxylin. (Erdmann.)

Hæmatoxylin thus prepared has more or less of a yellow colour, but by recrystallisation from water containing a little sulphite of ammonium, it may be obtained in colourless crystals. (Hesse.)

Hæmatoxylin forms two kinds of crystals containing respectively 3 and 1 at. water. The trihydrated crystals, $C^{16}H^{14}O^{6}.3H^{2}O$, obtained as above, belong to the dimetric system. Ordinary combination $\infty P\infty \,.\, P$, with $P\infty$ subordinate. Length of principal axis = 0·63 (nearly). Angle of the terminal edges of the primitive octohedron, $P = 124°$. The crystals are transparent, generally very brilliant, and sometimes of considerable length. They give off their water (15·1 per cent.) in vacuo at ordinary temperatures.

The *monohydrate*, $C^{16}H^{14}O^{6}.H^{2}O$ (containing 5·6 water), is obtained by leaving a solution supersaturated at mean temperature to stand for some time, in crystals of considerable size, with smooth and sometimes curved faces, and consisting, according to a preliminary determination by Naumann, of hemihedral trimetric combinations, $oP \,.\, \frac{P}{2} \,.\, m\breve{P}\infty$. The same hydrate is obtained in granular crystals, by pouring a solution of hæmatoxylin, supersaturated at the boiling heat, into a cold vessel containing a small quantity of solution of acid sulphite of ammonium. (Hesse.)

Dehydrated hæmatoxylin contains, according to Erdmann's analyses, 63·17—63·66 per cent. carbon, and 4·65—4·70 hydrogen, whence Erdmann deduced the formula $C^{40}H^{17}O^{15}$. Gerhardt, however (*Traité*, iv. 299), suggested the more probable formula, $C^{16}H^{14}O^{6}$, which requires 63·5 per cent. C, 4·5 H, and 31·9 O.

Hæmatoxylin dissolves slowly and sparingly in cold *water*, easily in *alcohol* and *ether* (Erdmann). It dissolves in a saturated solution of *borax* more easily than in pure water, forming a neutral or slightly acid liquid, which exhibits a bluish fluorescence, and from which the borax is not precipitated by alcohol. This solution, mixed with hydrochloric, acetic, or sulphuric acid, solidifies to a dense mass, in which granular crystals of monohydrated hæmatoxylin quickly form; but on addition of solution of chloride of sodium, potassium, or ammonium, ferrocyanide of potassium, or acid sulphite of ammonium, it deposits hæmatoxylin as a white amorphous mass. When acid sulphite of ammonium is added by drops to the same solution, hæmatoxylin is at first deposited in the form of an amorphous gummy precipitate, which re-dissolves on boiling the liquid, and reappears on cooling; but on continuing the addition of the acid sulphite to the syrupy liquid, a point is at length attained at which the amorphous hæmatoxylin disappears, and crystals of hæmatoxylin are soon afterwards obtained. When amorphous hæmatoxylin is dissolved in boiling water, and a drop of hydrochloric acid added to the solution, crystals of hæmatoxylin, generally the monohydrate, are soon deposited. (Hesse.)

Hæmatoxylin dissolves abundantly in a warm solution of *hyposulphite of sodium*, forming a purple liquid, which deposits amorphous hæmatoxylin on cooling. It dissolves with some difficulty in solution of *chloride of sodium*, more easily in a saturated solution of *chloride of barium* (this solution at first depositing crystals of the trihydrate, which gradually give place to those of the monohydrate), very abundantly in solution of *ordinary phosphate of sodium*, forming a liquid which behaves like the solution of hæmatoxylin in borax above mentioned, excepting that it exhibits a basic reaction. (Hesse.)

Hæmatoxylin has a strongly saccharine taste, like that of liquorice, very persistent, and without astringence or bitterness. Its solutions turn the plane of polarisation to the right. It reduces cupric oxide in an alcoholic solution containing alkali.

An aqueous solution of hæmatoxylin is not altered by contact with pure air or oxygen gas; but if the slightest trace of *ammonia* is present in the air, the liquid acquires a yellowish red colour, arising from the formation of hæmateate of ammonium; probably thus:

$$C^{16}H^{14}O^6 + O + NH^3 = C^{16}H^9(NH^4)O^6 + 2H^2O.$$

Hæmatoxylin melts in its water of crystallisation when moderately *heated*, and is completely carbonised at higher temperatures. *Chlorine* converts it into an uncrystallisable mass. With *nitric acid* it forms oxalic acid. *Sulphuric* and *hydrochloric acids* have but little action upon it.

With *bases*, hæmatoxylin forms compounds which, on exposure to the air, are converted into hæmateates. *Baryta-water*, added to a solution of hæmatoxylin freed from air by boiling, forms a white precipitate which soon turns blue if the air has access to it. *Potash* imparts to the solution a violet colour, quickly changing to purple and brown. With acetate of *lead*, neutral or basic, the solution yields a white precipitate, which quickly turns blue; with *cupric* acetate or sulphate, a greenish grey precipitate, which soon becomes dark blue with a coppery lustre. *Dichloride of tin* forms a rose-coloured precipitate, which does not change colour. *Iron alum* forms, after a while, a slight blackish violet precipitate. *Common alum* colours the solution light red, but does not produce a precipitate. *Chloride of barium* first colours the liquid red, and then forms a red precipitate. The solution of hæmatoxylin quickly reduces nitrate of *silver* and chloride of *gold*.

HÆMIN. A crystallised, intensely red substance, which may be prepared from blood in various ways, but is difficult to obtain in the pure state, and has therefore not been analysed. The crystals are obtained immediately on mixing blood, either fresh or boiled, with strong acetic acid. No crystals are formed, however, when blood coagulated by boiling is first washed with water and then treated with acetic acid (Teichmann, Pfeufer and Henle's Zeitschr. f. rat. Medicin, iii. 357; viii. 141). According to Krauss (Jahresb. d. Chem. 1861, p. 792), human blood may be distinguished with certainty from that of the ox, sheep, pig, mouse, or poultry, by the characters of the hæmin-crystals obtained from it.

HAFREFJORDITE. Oligoclase from Hafrefjord, in Iceland.

HAIDINGERITE. A hydrated arsenate of calcium, $2Ca^2HAsO^4.3H^2O$, supposed to be from Baden or Joachimsthal, associated with pharmacolite. Occurs in minute crystals belonging to the trimetric system, mostly congregated in botryoïdal forms and drusy crusts. Specific gravity 2·848. Hardness 1·5 to 2·5. Lustre vitreous. Colour white. Streak white. Transparent or translucent. Sectile; their laminæ slightly flexible. (Dana, ii. 413.)

Crystals having the form and composition of haidingerite may be produced artificially by digesting carbonate of calcium at ordinary temperatures with excess of aqueous arsenic acid. (Debray, Ann. Ch. Phys. [3] lxi. 419.)

HAIR. Hair consists of a cylindrical tube clothed with minute scales, having their points directed towards the free extremity. The tube is filled with an oil, which gives the colour to the hair; in white hair this oil is colourless.

In the normal state hair is insensible, strongly electric, and a bad conductor of heat. In contact with the air, it swells and absorbs moisture, but does not putrefy. Chlorine first bleaches and then converts it into a resinous matter resembling turpentine.

Hair is insoluble in water. Heated with water in a sealed tube, it is decomposed, with liberation of sulphydric acid. A similar decomposition takes place with aqueous potash. Nitric acid turns it yellow, forming oxalic acid, sulphuric acid, and a peculiar bitter substance. Hydrochloric and sulphuric acids dissolve it, forming rose-coloured solutions. Alkalis dissolve it. Many salts and metallic oxides, and likewise certain organic substances, change the colour of red or white hair to black. A solution of nitrate of silver in ether, or the same salt mixed with lard, oil, slaked lime, or pyrogallic acid is commonly used for blackening hair.

Hair, when heated, becomes hard, swells and emits an odour of burnt horn, and in the open air, takes fire, burns with a bright flame, and leaves a residue of charcoal. By dry distillation it yields oily and ammoniacal products.

According to Von Laer, human hair contains 49·8 per cent. carbon, 6·4 hydrogen, 17·1 nitrogen, 5·0 sulphur, and 26·7 oxygen. It leaves by calcination from 0·32 to 1·85 per cent. of ash, consisting of 0·17 to 0·93 soluble matter, 0·658 to 0·390 oxide of iron, and 0·000 to 0·528 earthy salts. (Pelouze et Frémy, *Traité*, vi. 244.)

HAIR-SALT. A term applied to native *sulphate of aluminium*, $Al^4(SO^4)^3.9H^2O$, and to *iron-alum*, $Al^2Fe(SO^4)^2.12H^2O$, these salts sometimes occurring in delicate fibrous masses. (See ALUM and SULPHATES.)

HALLITE. Basic sulphate of aluminium, $2(Al^4O^3.SO^3).3H^2O$. (Syn. with WEBSTERITE.)

HALLOYSITE or **HALLOYTE.** A hydrated silicate of aluminium containing a larger proportion of water than ordinary clay, which it otherwise resembles. After drying in the air at ordinary temperatures, it retains nearly $2H^2O$, but by drying in the kiln, the proportion of water is reduced to nearly that of common clay, viz. $Al^4O^3.SiO^3 + H^2O$. It occurs in white, soft, smooth masses, with conchoïdal waxy fracture, adhering to the tongue, opaque or translucent at the edges only. When immersed in water, it does not fall to pieces but becomes more translucent. It is readily decomposed by sulphuric acid. The following are analyses :—

	Berthier.				Boussingault.	
	a 1.	*a* 2.	*b* 1	*b* 2.	*c* 1.	*c* 2.
Alumina	35·49	32·4	39·06	34·0	39·4	35
Silica	47·75	43·6	44·94	39·5	44·9	40
Water	16·76	23·0	16·00	26·5	15·7	25
	100·00	99·0	100·00	100·0	100·0	100

	Oswald.	Dufrénoy.	
	d.	*e.*	*f.*
Alumina	35·00	33·66	32·45
Silica	40·25	40·66	43·10
Water	24·25	24·83	22·30
Magnesia	0·25		1·70
	99·75	99·15	99·55

a, from Housscha, near Bayonne; (1) kiln-dried; (2) air-dried;—*b*, from Anglena, near Liége; (1) kiln-dried; (2) air-dried;—*c*, from Guateque, in New Granada; (1) dried at 100° C.; (2) air-dried; this specimen contained a trace of sal-ammoniac;—*d*, from Upper Silesia, containing a trace of manganese;—*e*, from La Vouth;—*f*, from Thiviers. (Gm. iii. 417.)

HALOGEN. The electro-negative radicle of a haloïd-salt.

HALOÏD SALTS. Berzelius applied this term to salts consisting of a metal united with an electro-negative radicle, viz. *chlorides*, *bromides*, *iodides*, *cyanides*, &c., designating by the term, AMPHID-SALTS, those which were supposed to result from the union of two binary compounds containing a common element, viz. the oxygen-salts, sulphur-salts, selenium-salts, and tellurium-salts. The distinction between these two classes of salts is no longer retained, but the term *haloïd* is still occasionally applied to the chlorides, bromides, iodides, fluorides, and cyanides.

HALOTRICHINE. A silky iron-alum, from the Solfatara, near Naples. (See SULPHATES).

HALOTRICHITE. A name applied sometimes to native iron-alum, sometimes to native hydrated sulphate of aluminium. (See SULPHATES.)

HAMATHIONIC ACID. An acid produced by the action of sulphuric acid on euxanthic acid. Its composition has not been exactly determined. The barium-salt contains 31·4 per cent. baryta; the lead-salt, 61·6 to 62·4 oxide of lead. (See EUXANTHIC ACID, ii. 610.)

HAMPSHIRITE. (See STEATITE.)

HARDNESS OF MINERALS. A harder body is distinguished from a softer, either by attempting to scratch one with the other, or by trying each with a file. To give a definite character to the results thus obtained, Mohs introduced a scale of hardness, consisting of ten minerals, gradually increasing in hardness from 1 to 10, viz.:

1. *Talc:* common laminated, light-green variety.
2. *Gypsum:* a crystallised variety.
3. *Calc-spar;* transparent variety.
4. *Fluor-spar:* crystalline variety.
5. *Apatite:* transparent variety.

5·5 *Scapolite:* crystalline variety.
6. *Felspar:* (orthoclase); white cleavable variety.
7. *Quartz:* transparent.
8. *Topaz:* transparent.
9. *Sapphire:* cleavable varieties.
10. *Diamond.*

The hardness of any given mineral may be determined by attempting to scratch it with some of the above minerals, or by trying to scratch a smooth surface of the successive members of the scale with a sharp corner of the substance to be examined; thus, if it scratches fluor-spar and is scratched by apatite, the hardness is between 4 and 5.

Or again, the relative hardness of a mineral may be determined by abrading one of its edges with a file. If the file abrades the mineral under trial with the same ease as fluor-spar, and produces an equal depth of abrasion with the same force, the hardness is said to be 4. If the mineral is abraded more easily than fluor-spar, but less easily than apatite, the hardness may be 4·25 or 4·5. In making these comparative trials, care must be taken to apply the file to edges of equal obtuseness. That part also of the specimen should be selected which has not been altered by exposure, and has the highest degree of transparency and compactness of structure. The pressure for determination should be rather heavy, and the file should be passed three or four times over the specimen.

Certain varieties of some minerals give a low degree of hardness under the file, owing either to impurities or imperfect aggregations of particles, whilst they scratch a harder species, showing that the particles are hard, but loosely aggregated; this peculiarity is exhibited by certain varieties of chiastolite, spinel, and sapphire.

Many minerals — kyanite and mica, for example—present different degrees of hardness on dissimilar faces. This inequality, like difference of colour, lustre, &c., in the faces, is confined to those primary forms which are developed upon unlike axes. (Dana, i. 180.)

HARMALA, ALKALOÏDS OF. (Gerh. iv. 9.—Handw. d. Chem. iii. 769.)—The seeds of the *Peganum Harmala*, a plant growing abundantly on the steppes of Southern Russia, especially in the Crimea, contain two organic bases called harmaline and harmine, probably in the form of phosphates; they are found in the seed-coating, not in the kernel. To obtain these alkaloïds, the pulverised seeds are exhausted in a percolating apparatus with water acidulated with acetic or sulphuric acid; and the brownish yellow extract, which contains the bases in the form of acetates, together with earthy phosphates, colouring matter, &c., is mixed with a solution of common salt, whereupon the hydrochlorates of the alkaloïds, which are insoluble in that liquid, are precipitated together with colouring matter. Nitrate of sodium may also be used instead of the chloride, provided care be taken that the extract of the seeds does not contain free sulphuric acid, as the nitric acid which would then be liberated might decompose the alkaloïds. The precipitate is collected on a filter, and washed with brine until the whole of the mother-liquor is removed; then dissolved on the filter with cold water, which leaves part of the colouring matter undissolved. The solution, treated with animal charcoal, and then at a temperature of 50° to 60° C. with ammonia added by small portions, yields the alkaloïds in the pure state, nearly the whole of the harmine being thrown down before the harmaline begins to separate. As soon as the latter body makes its appearance,—which may be known by examining the precipitate from time to time with the microscope, harmine crystallising in needles, while harmaline forms leafy scales,—the solution must be filtered hot, and the harmaline precipitated from it by ammonia.

The seeds contain about 4 per cent. of alkaloïds, of which one-third consists of harmine, and two-thirds of harmaline.

HARMALA RED. The seeds of harmala contain also a red colouring matter, which may be extracted by digesting them with alcohol for 8—14 days. It is insoluble in water, easily soluble in ether, and dissolves in all proportions in absolute alcohol. It unites with acids, forming red salts, and dyes wool or silk mordanted with acetate or sulphate of alumina, from the lightest rose-colour to the deepest scarlet. The colours do not, however, appear to be very fast. (Gm. xvi. 119.)

HARMALINE. $C^{13}H^{14}N^2O$.—Discovered by Göbel in 1837 (Ann. Ch. Pharm. xxxviii. 363); afterwards more minutely examined by Fritzsche (*ibid.* lxiv. 360; lxviii. 351, 355; lxxii. 306; lxxxviii. 327). It is colourless when pure; if it has a yellowish or brownish tint, it may be purified by suspending it in water, adding acetic acid in sufficient quantity to dissolve it, filtering to separate colouring matter, then precipitating with chloride or nitrate of sodium, or hydrochloric acid, washing the precipitate on a filter with a dilute solution of the reagent employed, dissolving it in tepid water, treating the solution with animal charcoal till it exhibits a light yellow colour, and precipitating by caustic potash.

Harmaline crystallised from alcohol forms octahedrons belonging to the trimetric system, modified by the faces $\infty\breve{P}\infty$, $\infty\bar{P}\infty$, and $\breve{P}\infty$. Ratio of the vertical to the horizontal axes, 1 : 1·804 : 1·415. Angles of the terminal edges in P = 116° 34′ and 131° 18′; of the lateral edges in the same = 83° 54′. It is sparingly soluble in water and ether, moderately soluble in cold alcohol, and very freely in boiling alcohol. It has a faint bitter taste; and colours the saliva yellow.

Harmaline, when heated, melts, gives off white vapours and becomes carbonised. Heated in a tube, it yields a white mealy sublimate. Oxidising agents, under certain circumstances, convert it into a red colouring matter, insoluble in water, soluble in alcohol. By some oxidising agents, however, harmaline is converted into harmine by loss of 2 at. of hydrogen; this change takes place when the acid chromate of harmaline is heated to 120° C., or when harmaline is heated with hydrochloric acid and alcohol, to which a little nitric acid is added. When nitrate of harmaline is heated with alcoholic hydrochloric acid, the harmaline is converted into harmine. Harmaline, boiled with excess of *nitric acid*, yields, first, nitroharmaline, then, by longer boiling, nitroharmine: with boiling *nitromuriatic acid*, it forms chloronitroharmine.

The salts of harmaline are yellow, have a bitter taste, and are for the most part easily soluble and crystallisable.

The *acetate* is obtained by spontaneous evaporation of a solution of harmaline in acetic acid, in the form of a syrup which becomes crystalline after a while. A solution of the acetate, mixed with acid carbonate of potassium, yields *acid carbonate of harmaline*, in the form of a precipitate composed of fine needles. The neutral alkaline carbonates either form no precipitate with the salts of harmaline, or merely throw down the base.

The *neutral chromate* is a sparingly soluble, yellow, crystalline salt, which may be obtained by adding acetate of harmaline drop by drop to a solution of neutral chromate of potassium, saturated in the cold, filtering from the precipitate of harmaline first produced, and adding more acetate of harmaline to the filtrate. The *acid chromate*, $2C^{13}H^{14}N^2O.H^2O.2Cr^2O^3$, is produced by adding acid chromate of potassium to a dilute solution of harmaline, and separates immediately in oily drops, which, after a while, become crystalline. When heated to 120° C., it is rapidly decomposed, yielding a sublimate of *harmine* and leaving a dark-coloured residue containing chromium.

The *hydrochlorate*, $C^{13}H^{14}N^2O.HCl.2H^2O$, forms long prismatic needles containing 12·3 per cent. water of crystallisation. It is moderately soluble in water and in alcohol. The *chloroplatinate*, $C^{13}H^{14}N^2O.HCl.PtCl^2$, is a yellow precipitate.

The *hydrocyanate* forms a peculiar alkali. The *hydroferrocyanate* is a brick-red crystalline powder; the *hydroferricyanate* forms long dark green prisms. The *sulphocyanate* forms silky needles, sparingly soluble in cold, more soluble in boiling water.

Nitrate of harmaline, obtained by precipitating the acetate with dilute nitric acid or nitrate of ammonium, forms needles sparingly soluble in pure water, and almost insoluble in water containing nitric acid.

Oxalates.—When aqueous oxalic acid is boiled with excess of harmaline, crystals of the neutral salt separate on cooling; and oxalic acid, added to the solution of these crystals, precipitates the acid oxalate of harmaline.

Sulphates.—By digesting dilute sulphuric acid with excess of harmaline, and evaporating the filtrate, the neutral sulphate is obtained as a yellow resin, which, when left over oil of vitriol, changes to a radio-crystalline mass.

Sulphite.—The solution of harmaline in aqueous sulphuric acid dries up to a yellow resin, exhibiting no traces of crystallisation.

Sulphydrate.—By mixing concentrated solutions of sulphydrate of ammonium and acetate of harmaline, slender prisms are obtained which quickly decompose on exposure to the air, after separation of the mother-liquor.

Hydrocyan-harmaline, $C^{14}H^{15}N^3O = C^{13}H^{14}N^2O.HCy$, is a base containing the elements of harmaline and hydrocyanic acid. It is obtained by dissolving harmaline in dilute boiling hydrocyanic acid and filtering hot, being then deposited in crystals on cooling; or by pouring a solution of cyanide of potassium into a solution of a salt of harmaline, or caustic potash into a solution of a salt of harmaline previously mixed with hydrocyanic acid. From aqueous solutions it is deposited in amorphous flocks, which give off hydrocyanic acid when dried in the air; the decomposition may, however, be prevented by dissolving the powder, while yet moist, in hot alcohol. If it still contains harmaline, it may be purified by suspending it in water and adding acetic acid, which readily dissolves the harmaline, but exerts little or no action on the hydrocyan-harmaline.

This base, when pure, forms thin rhomboïdal tables, which, when dry, undergo no alteration by exposure to the air, or in vacuo, or even at 100° C. At a higher temperature, or when boiled with water or alcohol, it is resolved into harmaline and hydrocyanic acid. Suspended in water and boiled with a large excess of nitric acid, it is decomposed, giving off red vapours, and yielding a purple solution which deposits non-crystalline grains of a fine red colour, changed to green by ammonia. Hydrocyan-harmaline, heated with hydrochloric acid and chloride of potassium, yields a resinous product.

The salts of hydrocyan-harmaline are even less stable than those of harmaline. The base does not appear to combine with all acids. The hydrochlorate, $C^{13}H^{14}N^2O.CyH.HCl$, is a crystalline powder composed of small octahedrons with a rhombic base and secondary faces, whereas hydrochlorate of harmaline, when examined by the microscope, appears like an aggregation of long yellow prisms. The *nitrate* and *sulphate* are also crystalline.

Nitroharmaline. $C^{13}H^{13}N^3O^3 = C^{13}H^{12}(NO^2)N^2O$. *Chrysoharmine.*—This body, which is derived from harmaline by the substitution of 1 at. nitryl, NO^2, for 1 at. hydrogen, may be prepared:—1. By suspending 1 pt. of harmaline in 6 or 8 pts. of alcohol of 80 per cent., adding 2 pts. of strong sulphuric acid, and, when the solution is complete, 2 pts. of moderately concentrated nitric acid; heating the mixture on the water-bath; and as soon as the reaction, which is very brisk, is over, cooling it quickly to prevent secondary decompositions. The liquid then deposits sulphate of nitroharmaline, which is to be washed with alcohol containing sulphuric acid, then dissolved in warm water, and precipitated by dilute potash or ammonia. If the nitroharmaline thus precipitated contains harmine or undecomposed harmaline, it may be freed therefrom by means of sulphurous acid, which forms a sparingly soluble salt with nitroharmaline, but very soluble salts with the other two bases.—2. By a process exactly similar to that which will be hereafter described for the preparation of nitroharmine, excepting that the nitric acid used must be weaker, viz. of specific gravity 1·12 instead of 1·40.

Nitroharmaline, precipitated from its salts by an alkali, is an orange-coloured powder composed of microscopic prisms; larger crystals are deposited from the alcoholic solution. It is but sparingly soluble in cold water, to which, however, it imparts a yellow colour; boiling water dissolves it much more freely. It is more soluble in alcohol than harmine or harmaline; sparingly soluble in cold ether, more soluble in hot ether. It dissolves in oils, both fixed and volatile; also in hot rock-oil. It melts at 120° C.

Heated with ammoniacal salts it decomposes them, expelling the ammonia. Nitric acid converts it into nitroharmine.

The salts of nitroharmaline are yellow. The *hydrochlorate*, $C^{16}H^{12}(NO^2)N^2O.HCl$, crystallises in small prisms; its solution, mixed with dichloride of platinum, yields the *chloroplatinate*, $C^{13}H^{12}(NO^2)N^2O.HCl.PtCl^2$, as a yellow precipitate, which ultimately assumes the form of minute prisms.

The *nitrate* crystallises in yellow needles, rather sparingly soluble in water, especially if it contains a little nitric acid. A perfectly neutral solution of this salt, mixed with ammoniacal nitrate of silver, yields a yellowish red flocculent precipitate, consisting of *argento-nitroharmaline*, $C^{13}H^{12}Ag(NO^2)N^2O.H^2O$.

A compound of *nitroharmaline with nitrate of silver* is obtained in light yellow crystalline flakes on mixing an alcoholic solution of nitroharmaline with nitrate of silver.

The *neutral sulphate* is obtained as a crystalline precipitate on saturating a solution of the acetate with sulphate of ammonium. The *acid sulphate*, $C^{13}H^{12}(NO^2)N^2O.H^2SO^4$, is produced by dissolving the base in excess of sulphuric acid, mixed with alcohol, or by dissolving it in strong sulphuric acid, and pouring the solution, drop by drop, into cold water. It is a pale yellow crystalline powder, nearly insoluble in cold water.

The *sulphite* is very little soluble in cold water, especially if acidulated with sulphurous acid.

The *acetate* is soluble; the *oxalate* crystallisable. The *hydroferrocyanate* is a yellow crystalline precipitate. The *hydroferricyanate* separates in oily drops, which solidify, after a while, to a crystalline powder. The *sulphocyanate* forms sparingly soluble microscopic needles.

Hydrocyano-nitroharmaline, $C^{13}H^{12}(NO^2)N^2O\ CyH$, is obtained by dissolving nitroharmaline in a hot alcoholic solution of hydrocyanic acid; also, by leaving a concentrated solution of acetate of nitroharmaline, mixed with hydrocyanic acid, to evaporate; or by adding ammonia to a salt of nitroharmaline containing hydrocyanic acid. It forms slender yellow needles, which give off the odour of ammonia when moist, but are permanent when dry. By boiling with water, it is resolved into nitroharmaline and hydrocyanic acid. Decomposed also by strong ammonia or potash. It dissolves in strong sulphuric acid, and the solution, poured into a small quantity of water, yields needles, apparently consisting of an insoluble sulphate.

HARMINE. $C^{13}H^{12}N^2O$. (Fritzsche, *loc. cit.*, p. 7.)—This alkali, which contains 2 at. H less than harmaline, may be obtained either directly from the seeds of *Peganum harmala*, in the manner already described, or as a product of the oxidation of harmaline. Acid chromate of harmaline, heated to 120° C., decomposes suddenly with evolution of heat, and produces harmine, part of which volatilises and condenses on the sides of the vessel. A better process is to heat harmaline with a mixture of equal parts of hydrochloric acid and alcohol, to which a little nitric acid is added. The conversion of the harmaline is complete soon after the liquid begins to boil, and on cooling, hydrochlorate of harmaline is abundantly deposited in slender needles. The solution of this salt, decomposed by ammonia, yields the base.

Harmine forms rhomboïdal prisms of 124° 18′, and 55° 42′, nearly insoluble in *water*, very sparingly soluble, at ordinary temperatures, in *alcohol* and in *ether*. It is a weaker base than harmaline; nevertheless it expels ammonia from its salts at the boiling heat.

The salts of harmine are colourless, and mostly crystalline; their solutions have a yellow tint when concentrated, bluish when dilute. Alkalis and alkaline carbonates decompose them, precipitating the base.

The *acid chromate*, $2C^{13}H^{12}N^2O.H^2O.2Cr^2O^3$, is always formed on mixing an acid solution of harmaline with a soluble chromate. It is decomposed by heat, yielding a peculiar base.

The *hydrochlorate*, $C^{13}H^{12}N^2O.HCl$, forms needles containing 12·38 per cent. water, which they give off at 100° C. From alcohol, the salt is deposited in the anhydrous state. The *chloroplatinate*, $C^{13}H^{12}N^2O.HCl.PtCl^2$, is a flocculent precipitate, becoming crystalline when heated. The *chloromercurate* is deposited as a curdy precipitate from cold solutions, and crystalline from hot solutions. The *hydrobromate* and *hydriodate* resemble the hydrochlorate.

The *hydroferrocyanate* and *hydroferricyanate* are obtained as yellow precipitates.

The *nitrate* forms yellow needles, sparingly soluble in cold water, still less in water acidulated with nitric acid.

The *neutral oxalate* is a crystalline precipitate. The *acid oxalate*, $C^{13}H^{12}N^2O.C^2H^2O^4.H^2O$ forms radiating needles, containing 5·67 per cent. water, which they give off at 100° C.

The *neutral sulphate*, $2C^{13}H^{12}N^2O.H^2SO^4.2H^2O$, obtained by dissolving an excess of harmine in dilute sulphuric acid and evaporating, forms concentrically grouped needles containing 6·57 per cent. of water. The *acid sulphate*, $C^{13}H^{12}N^2O.H^2SO^4$, obtained by adding excess of sulphuric acid to a solution of harmaline in boiling alcohol, forms crystals similar in form, but anhydrous.

The *sulphocyanate* is obtained by precipitation in yellow needles.

Substitution-derivatives of Harmine.

Dichlorharmine. $C^{13}H^{10}Cl^2N^2O$. (Fritzsche, Petersb. Acad. Bull. v. 12.)—Produced by the action of hypochlorous acid on harmine. To prepare it, a very dilute solution (containing 1½ to 2 per cent.) of hydrochlorate of harmine is heated to boiling; 10 to 15 per cent. of strong hydrochloric acid is then added to it, and afterwards, the solution being still kept boiling, chlorate of potassium is thrown in, by small quantities at a time, until the brownish red colour which the liquid assumes at first, is changed to pure yellow. The ebullition is maintained a little while longer, so as to destroy a coloured product; the solution is then allowed to cool; and the crystals of dichlorharmine which separate are washed with dilute hydrochloric acid, or with solution of chloride of sodium, and purified by crystallisation from alcohol, or re-solution in water and precipitation by hydrochloric or nitric acid. On redissolving the hydrochlorate of dichlorharmine in a large quantity of hot water, and boiling it for several hours with a great excess of soda-ley, crystals of dichlorharmine are deposited, which must be recrystallised from alcohol.

Dichlorharmine forms soft white needles, insoluble in cold, very slightly soluble in boiling water. It dissolves in *alcohol*, *ether*, *benzene*, and *sulphide of carbon*, much more easily when heated than in the cold.

Dichlorharmine forms a compound with *iodine*, corresponding to di-iodide of nitroharmine (p. 11), and containing 46·45 per cent. iodine.

With *acids* it forms crystallisable salts, which, like those of harmine, are very difficultly soluble in water containing acids or salts. The mono-acid (neutral) salts are decomposed to a certain extent, with separation of dichlorharmine, when a large quantity of water is poured upon them. Ammonia throws down dichlorharmine from their solutions, as an amorphous, colourless jelly; solution of soda acts in the same way, but in this case the precipitate becomes crystalline when long boiled with a great excess of soda solution. Dichlorharmine displaces a trace of ammonia from a boiling solution of sal-ammoniac; part of the dissolved dichlorharmine separates out on cooling, but the rest only on addition of ammonia to the filtrate.

Hydrochlorate of Dichlorharmine is obtained by dissolving the base in water containing hydrochloric acid, and precipitating by excess of hydrochloric acid. It crystallises from water in needles, from alcohol in larger crystals; chloride of sodium separates it from its solution in the form of a jelly which turns to needle-shaped crystals. It contains 2 at. water, which it gives off at 100° C., but reabsorbs 1 at. if exposed to moist air. When heated much above 100°, it becomes yellow and loses hydrochloric acid; between 180° and 200° it melts to a brown-yellow liquid, which dissolves in water and contains a newly formed base.

The *nitrate* is precipitated as a jelly, which afterwards changes to crystalline needles, by addition of excess of nitric acid to a solution of dichlorharmine in water containing nitric acid. It is anhydrous and less soluble in water than the hydrochlorate. When melted it gives off acid vapours and yields a brown mass, from the solution of which in aqueous alkalis acids throw down brown flocks.

Nitrate of dichlorharmine precipitates from *oxide of argentammonium*, a pale greenish jelly, containing silver. When hydrochlorate of dichlorharmine is mixed with nitrate of silver, a jelly is precipitated, without formation of chloride of silver, but, on adding nitric acid to the jelly, chloride of silver is formed.

Nitroharmine. $C^{13}H^{11}(NO^2)N^2O$. *Nitroharmidine.* (Fritzsche, Petersb. Acad. Bull. xii. 33, 225; Ann. Ch. Pharm. lxviii. 328; xcii. 330.)—Produced by the action of nitric acid on harmaline or nitroharmaline. It does not appear to be formed by the action of nitric acid on harmine. To prepare it, 1 pt. of harmaline is dissolved in 2 pts. of water, and the requisite quantity of acetic acid, and to the solution 12 pts. of nitric acid of specific gravity 1·40 are added in a thin stream. A violent evolution of red vapours takes place; and if the liquid be kept in a state of ebullition till the action is over, then cooled quickly, and treated with excess of caustic alkali, nitroharmine is deposited in the form of a deep yellow precipitate, while a resinous matter, formed at the same time, remains in solution. The product is purified by converting it into a hydrochlorate, and decomposing that salt with ammonia. Nitroharmine forms yellow needles, tasteless, sparingly soluble in cold, more soluble in boiling water. From boiling alcohol it separates in deep yellow octahedrons, which soon change into needles. Ether dissolves it but sparingly. It dissolves in rock-oil and in coal-tar naphtha. Heated with a solution of sal-ammoniac, it slowly eliminates ammonia. It unites with iodine, but is decomposed by chlorine and bromine.

The salts of nitroharmine have a slightly bitter taste, and mostly crystallise in yellow needles. The *hydrochlorate*, $C^{13}H^{11}(NO^2)N^2O.HCl + 2H^2O$, obtained by adding hydrochloric acid in excess to a solution of the base in acetic acid, or in hot water acidulated with a few drops of hydrochloric acid, crystallises in slender needles, which may be purified by recrystallisation from boiling alcohol. The *chloroplatinate* is soluble and crystallises in needles.

The *neutral nitrate* is but sparingly soluble in water, still less in dilute nitric acid: hence nitric acid gradually precipitates nitroharmine from the solutions of its other salts. It crystallises in yellow needles, which, if left in the acid liquor, gradually change to granular and rhomboïdal crystals of a deeper yellow colour. There appears also to be a *basic nitrate*, somewhat more soluble in water.

The hydrocyanate does not appear to exist by itself, but a double compound of *hydrocyanate of nitroharmine and mercuric cyanide* is deposited in granular crystals when cyanide of mercury is added to a boiling solution of acetate of nitroharmine and the liquid left to cool.

The *hydroferrocyanate* and *hydroferricyanate* are obtained by precipitation, the former in brown microscopic prisms, the latter in yellow grains. The *sulphocyanate* forms nearly colourless needles, sparingly soluble in cold, more soluble in hot water.

Di-iodide of Nitroharmine, $C^{13}H^{11}(NO^2)N^2O.I^2$, separates in yellowish brown agglomerated microscopic needles, on mixing the boiling solutions of iodine and nitroharmine in alcohol or coal-tar naphtha. It is nearly insoluble at ordinary temperatures in water, alcohol, ether, and coal-tar naphtha; slightly soluble at higher temperatures. It may be heated to 100° C. without decomposition. It is resolved into iodine and nitroharmine by boiling with alcohol, and more quickly with dilute sulphuric acid. It appears to form a crystalline salt with hydrochloric acid. It dissolves also in acetic and hydrocyanic acids, and these solutions yield crystalline compounds.

BROMONITROHARMINE. $C^{13}H^{10}BrN^3O^3 = C^{13}H^{10}Br(NO^2)N^2O$. *Bromonitroharmidine.*—When bromine-water is added to a very dilute solution of a salt of nitroharmine, the smell of bromine disappears immediately, and on addition of ammonia, bromonitroharmine is precipitated and may be purified by recrystallisation from alcohol. It resembles chloronitroharmine, forms salts with acids, and unites with bromine and iodine.

The *dibromide*, $C^{13}H^{10}BrN^3O^3.Br^2$, is formed on adding bromine-water in moderate excess to a solution of bromonitroharmine in weak alcohol, and separates on cooling and stirring the liquid, in yellow microscopic needles.

Chloronitroharmine. $C^{13}H^{10}ClN^3O^3 = C^{13}H^{10}Cl(NO^2)N^2O$. *Chloronitroharmidine.* (Fritzsche, Petersb. Acad. Bull. xii. 225; Ann. Ch. Pharm. xcii. 330).—Produced by the action of chlorine on nitroharmine, or of nitromuriatic acid on harmaline.

Preparation.—1. When chlorine-water is added to aqueous hydrochlorate or acetate of nitroharmine, or chlorine gas is passed into the solution till the smell of chlorine becomes permanent, chloronitroharmine separates in the form of a jelly. If the action of the chlorine be too long continued, a yellow resin is produced. The mixture is heated to boiling, and the resulting solution is precipitated by the cautious addition of ammonia, drop by drop, with constant stirring. A more or less crystalline product is thus obtained, whereas, from cold solutions, a jelly is precipitated, which is difficult to wash.—2. A solution of 1 pt. harmaline in 2 pts. water and the requisite quantity of acetic acid, is poured into 12 pts. of boiling nitric acid of specific gravity 1·40, and 2 pts. of fuming hydrochloric acid are added to the mixture; or the harmaline solution is poured into the boiling mixture of the two acids. The liquid becomes red-brown, froths up strongly, and evolves a volatile substance which attacks the eyes, but deposits nothing but resin on cooling. In order to separate the dissolved chloronitroharmine, a solution of sal-ammoniac, cooled by placing lumps of ice in it, is poured into the liquid; this is diluted with about an equal bulk of water; and caustic soda is then added, until it smells strongly of ammonia, whereby an abundant precipitate of impure chloronitroharmine is thrown down. The product is washed with dilute hydrochloric acid and heated with water; the solution freed by filtration from undissolved resin, and precipitated by gradual addition of ammonia; and the precipitate purified by crystallisation from hot alcohol. The crude chloronitroharmine may also be dissolved in boiling water, with addition of just the necessary quantity of nitric acid, and precipitated as nitrate from the cooled filtrate by addition of nitric acid in excess; this salt, after being washed, may be dissolved in hot water, and pure chloronitroharmine precipitated from the boiling filtered solution by means of caustic ammonia.

Chloronitroharmine forms a bright yellow, brittle mass, composed of very fine needles, which cannot be distinctly perceived, even under a magnifying power of 300. Ammonia precipitates it from cold solutions, as an almost transparent, deep yellow, very bulky jelly, which shrinks very much on drying. It is tasteless in the solid state, slightly bitter and rough in solution. It gives off 11·4 per cent. water at 100° C. (2 at. = 10·98 per cent.), and becomes orange-yellow. It dissolves but slightly in cold *water;* more abundantly in boiling water, forming a yellow solution; with moderate facility in boiling alcohol; slightly in ether; abundantly in boiling coal-tar naphtha, and in rock-oil.

Chloronitroharmine dried at 100° C. leaves a reddish-yellow residue when alcohol or coal-tar naphtha is poured upon it, but dissolves completely when boiled with dilute nitric acid.—*Solution of iodine* converts it into di-iodide of chloronitroharmine. When mixed with solution of iodide of potassium, and then with nitric acid, it deposits a deep blue precipitate.

Chloronitroharmine unites with acids, forming yellow salts. When boiled with solution of sal-ammoniac, it slowly displaces a trace of ammonia.

The *hydrochlorate*, obtained by adding hydrochloric acid in excess to a solution of the base in hot alcohol, forms fine capillary crystals moderately soluble in water. It is precipitated from its aqueous solution by a large excess of hydrochloric acid, as a yellow jelly; by chloride of sodium in white flocks. On mixing the hot alcoholic solutions of this salt and dichloride of platinum, *chloroplatinate of chloronitroharmine*, $C^{13}H^{10}ClN^3O^3.HCl.PtCl^2$, is deposited on cooling in fine yellow prisms.

The *nitrate* forms stellate groups of slender needles. A perfectly neutral solution of this salt mixed with ammonio-nitrate of silver, yields a precipitate consisting of a compound of chloronitroharmine with nitrate of silver.

Sulphates.—A solution of chloronitroharmine in warm alcohol containing sulphuric acid deposits the *neutral sulphate* on cooling, in spherical groups of capillary needles. From a hot aqueous solution the salt is deposited in light yellow gelatinous flocks. The *acid sulphate* separates slowly in needles from a hot concentrated alcoholic solution of the neutral salt mixed with excess of sulphuric acid.

Di-iodide of Chloronitroharmine, $C^{13}H^{10}ClN^3O^3.I^2$, separates in slender needles resembling di-iodide of nitroharmine, from a mixture of the hot solutions of iodine and chloronitroharmine in alcohol or in coal-tar naphtha. It is more soluble in alcohol than the di-iodide of nitroharmine, and dissolves easily in warm alcoholic hydrocyanic acid, separating in rounded granules on cooling.

HARMOTOME. This term includes two isomorphous mineral species, identical in crystalline form, viz.: *Baryta-harmotome*, and *Lime-harmotome.*

Baryta-harmotome, also called *Cross-stone*, *Staurolite*, *Andrealite*, *Andreasbergolite*, *Morvenite.*—Crystals belonging to the trimetric system, being generally rectangular prisms with four-sided summits set upon the lateral edges. Ordinary combination, P . $\infty\breve{P}\infty$. $\infty\bar{P}\infty$. $\breve{P}\infty$ (like *fig.* 528), often without $\breve{P}\infty$. Ratio of the axes: $a : b : c = 0{\cdot}9781 : 1 : 0{\cdot}684$. For P, the angle of the terminal edges in the brachydiagonal section = 121° 28′, in the macrodiagonal section, = 120° 1′; and the angle of the lateral edges (in a section parallel to the base) is 88° 44′. Cleavage most distinct parallel to $\infty\breve{P}\infty$. The crystals are generally twins, inserted crosswise into one another, as shown in *fig.* 529, in which the faces $\infty\bar{P}\infty$ are denoted by *n*, and $\infty\breve{P}\infty$ by *m*. For distinctness, the faces of one of the crystals are shaded (Kopp, *Krystallographie*, p. 263). Rarely massive. Specific gravity = 2·39 to 2·498. Hardness = 4·5. Lustre vitreous. Colour white, passing into grey, yellow, red, or brown. Streak white. Subtransparent to translucent. Fracture uneven, imperfectly conchoïdal. Brittle. Melts without intumescence before the blowpipe, forming a white globule. When finely pounded it is decomposed completely, though with difficulty, by hydrochloric acid.

Fig. 528.

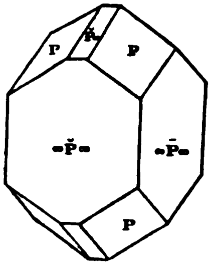
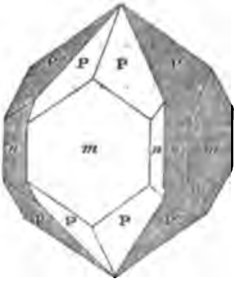


Fig. 529.



The following are analyses of baryta-harmotome:—*a*, from Oberstein; *b*, from Strontian (Köhler, Pogg. Ann. xxxvii. 561); *c*, from Strontian (Connell, Ed. N. Phil. J., 1832, July, p. 33); *d*, *Morvenite*, from the same (Damour, Ann. Min. [4] ix. 339); *e*, from Andreasberg; *f*, from Strontian (Rammelsberg, *Mineralchemie*, p. 821).

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
SiO^2	46·65	46·10	47·04	47·60	48·74	48·49
Al^4O^3	16·54	16·41	15·24	16·39	17·65	16·35
Fe^4O^3	. .	. .	0·24	0·65		
Ba^2O	19·12	20·81	20·85	20·86	19·22	20·08
Ca^2O	1·10	0·63	0·10			
K^2O Na^2O	1·10	0·90	1·72	1·55	. .	2·07
H^2O	15·25	15·11	14·92	14·16	14·66	13·00
	99·76	99·96	100·11	101·21	100·27	99·99

These analyses agree pretty nearly with the formula $Ba^2O.Al^4O^3.5SiO^2 + 5H^2O$ (Rammelsberg), which requires 46·65 per cent. silica, 15·56 alumina, 23·79 baryta, and 14·00 water (the other constituents being regarded as adventitious), and by substituting $al = \frac{2}{3}$ Al, and regarding 2 at. hydrogen as basic, this formula becomes $(Ba^2al^6H^2)Si^5O^{15} . 4H^2O$, which is reducible to $M^2SiO^3 . \frac{4}{5}H^2O$, the formula of a metasilicate.

The composition of the mineral has, however, been hitherto generally represented by the formula $BaO.Al^2O^3.3SiO^3 + 5HO$, or $2(Ba^2O.Al^4O^3).9SiO^2 + 10H^2O$; but this formula gives only 44 per cent. silica, which is considerably below that of all analyses which have been made of the mineral.

Baryta-harmotome occurs at Oberstein in Zweibrücken, in siliceous geodes; at Andreasberg in the Hartz; at Strontian in Argyleshire; in Norway on gneiss; and in simple crystals with analcime, in the amygdaloïd of Dumbartonshire. The variety called *Morvenite*, distinguished by the greater brilliancy of its crystals, is also found at Strontian. (Dana, ii. 323; Gm. iii. 446.)

Lime-harmotome or *Potash-harmotome*, *Phillipsite*, *Christianite*.—Isomorphous with the preceding, occurring also in twins. Specific gravity = 2·2 to 2·213. Hardness = 4 to 4·5. Lustre vitreous. Colour white, sometimes reddish. Streak uncoloured. Translucent—opaque. Before the blowpipe it intumesces slightly, gives off water, and melts to a translucent glass. Hydrochloric acid decomposes it easily, with separation of gelatinous silica.

The following are analyses of lime-harmotome:—*a*, from Annerode near Giessen

(Wernekink, Gilb. Ann. lxxvi. 171, 336); *b*, from Stempel near Marburg (L. Gmelin, Leonh. Zeitschr. f. Min. 1826, i. 8); *c*, from the same; *d*, from Habichtswalde, near Cassel (Köhler, Pogg. Ann. xxxvii. 561); *e*, from the Giant's Causeway (Connell, Edinb. Phil. J. xxxv. 373).

	a.	*b.*	*c.*	*d.*	*e.*
SiO^2	48·36	48·51	50·44	48·22	47·35
Al^4O^3	20·00	21·76	21·78	23·33	21·80
Fe^4O^3	0·41	0·99	. .	. .	3·70
Ca^2O	5·91	6·26	6·50	7·22	4·85
K^2O	6·41	6·33	3·95	3·89	5·55 Na^2O
Ba^2O	0·46				
H^2O	17·09	17·23	16·81	17·56	16·96
	98·64	101·08	99·48	100·22	100·21

The composition of lime-harmotome has been represented by several different formulæ. The quantities of calcium and potassium contained in it are somewhat variable, but its composition appears to be, for the most part, that which is expressed by the formula $\left.\begin{matrix}2Ca^2O\\K^2O\end{matrix}\right\}.3Al^4O^3.12SiO^2 + 15H^2O$ (50·2 per cent. SiO^2, 21·3 Al^4O^3, 7·0 Ca^2O, 6·5 K^2O, and 15·0 water), which, by substitution of *al* for $\frac{3}{4}$Al, as before, becomes $(Ca^2Kal^9)Si^6O^{18}.\frac{15}{2}H^2O$, and is reducible to the general formula $M^{12}Si^6O^{18}.\frac{15}{2}H^2O$, or $M^2SiO^3.\frac{5}{4}H^2O$, which is that of a metasilicate, and differs from the general formula of baryta-harmotome only in its amount of water.

Lime-harmotome occurs in the amygdaloïd of the Giant's Causeway, in large transparent crystals. It is also found in Iceland; among the Vesuvian lavas; in sheaf-like aggregations at Capo di Bove, near Rome; and in long radiating crystals at Aci Castello in Sicily, and other localities. (Dana, ii. 324; Rammelsberg, *Mineralchemie*, p. 811.)

HARRINGTONITE. See NATROLITE.

HARRISITE. A variety of cuprous sulphide, Ccu^2S, occurring in the Canton mine, Georgia, in crystals belonging to the regular system, and cleaving parallel to the faces of a cube (Shepard, Jahresb. d. Chem. 1857, p. 656). Genth (Sill. Am. J. [2] xxii. 449) regards it as a pseudomorph of copper-glance after galena.

HARTINE. $C^{10}H^{17}O$. *Psatyrin*.—A fossil resin resembling hartite. Massive, but crystallises from rock-oil in needles belonging to the trimetric system. White; destitute of taste and smell. Pulverises between the fingers. Melts at 210° C., and distils at 260°. Slightly soluble in ether. Gives, by analysis, 78·06 per cent. C, 10·92 H, and 11·02 O. It is found in the lignite of Oberhart, Austria. (Schrötter, Pogg. Ann. liv. 45.)

HARTITE. C^6H^5.—Another fossil resin from the lignite of Oberhart. Oblique prisms belonging to the monoclinic system. Cleavage only in traces. Specific gravity 1·046. Hardness = 1. White, with a somewhat greasy lustre. Translucent. Brittle. Melts at 74° C., and distils at higher temperatures. Dissolves easily in ether, less readily in alcohol, and crystallises from each solution by evaporation (Haidinger, Pogg. Ann. liv. 261). Gives, by analysis, 87·47 per cent. C and 12·05 H. (Schrötter.)

HATCHETTINE or *Mineral Tallow*, a fossil resin occurring in the coal measures of Glamorganshire; crystallised and amorphous in thin laminæ; like wax or spermaceti in consistence. Specific gravity 0·916 at 15·5° C. White and transparent, with nacreous lustre, but becomes black and opaque by long exposure. Greasy to the touch. Melts at 46° C. Distils without change when cautiously heated. Dissolves sparingly in boiling alcohol, and separates on cooling; sparingly also in cold ether, more easily in hot ether. Gives, by analysis, 85·9 per cent. carbon and 14·6 hydrogen (= 100·5). (Johnston, Phil. Mag. xii. 338.)

A similar substance is found at Rossitz, in Moravia. Specific gravity, 0·892. Hardness = 1. A variety from Loch Fyne, near Inverness, melts at 47° C. Another allied mineral from Merthyr Tydvil, melts at 76·6° C.

HAUERITE. Native disulphide of manganese, MnS, found at Kalinka, in Hungary. (See MANGANESE, SULPHIDES OF.)

HAUSMANNITE. Native manganoso-manganic oxide, $Mn^2O.Mn^4O^3$, or Mn^6O^4, found at Ilmenau in Thuringia, at Ihlefeld in the Hartz, and one or two other localities. (See MANGANESE, OXIDES OF.)

HAUYNE. A mineral consisting of silicate of aluminium, sodium, and calcium, with sulphate of calcium, occurring in the lavas of Vesuvius, on Somma, and on the basalt of Niedermendig, near Andernach, on the Rhine. It crystallises in rhombic dodecahedrons, with cleavage parallel to the faces, sometimes distinct; commonly in crystalline grains. Specific gravity 2·4 to 2·5. Hardness 5·5. Lustre varying from vitreous to greasy. Colour bright blue, occasionally asparagus-green. Streak bluish-white. Subtransparent to translucent. Fracture flat-conchoïdal to uneven. Before the blowpipe it decrepitates and fuses slowly to an opaque white or greenish-blue glass. Effervesces with borax, and forms a glass which is yellow when cold. The finely pulverised mineral dissolves completely in hydrochloric acid, the liquid depositing gelatinous silica when evaporated.

The composition of hauyne has been variously stated. From the analysis of the mineral from Mont Albano, Whitney (Pogg. Ann. lxx. 431) deduced the formula $3(Na^2O.Al^4O^6.2SiO^2) + 2(Ca^2O.SO^3)$, or $3(Na\mathit{al}^3)SiO^4.Ca^2SO^4$; from that of hauyne from Somma, Rammelsberg calculates the formula $2(Na^2O.Al^4O^6.2SiO^2) + (Ca^2O.SO^3)$, or $4(Na\mathit{al}^3)SiO^4.Ca^2SO^4$. The following table exhibits the numbers deduced from these formulæ, together with the results of the corresponding analyses:

Mont Albano. (Whitney.)	Calc.	Analysis.	*Somma.* (Rammelsberg.)	Calc.	Analysis.
$6SiO^2$ . .	32·20	32·48	$4SiO^2$ . .	34·29	34·06
$2SO^3$ . .	14·31	12·98	SO^3 . .	11·43	11·25
$3Al^4O^6$ . .	26·83	27·75	$2Al^2O^3$ . .	28·57	27·64
$2Ca^2O$ . .	10·02	9·96	Ca^2O . .	8·00	10·60
$3Na^2O$ . .	16·64	14·24	$2Na^2O$ . .	17·71	11·79
K^2O . .	. .	2·40	K^2O . . .	. .	4·96
	100·00	99·81		100·00	100·30

According to these formulæ, hauyne is allied to nosean, sodalite, and ittnerite, all of which are silicates of the form $M^2O.Al^4O^6.2SiO^2$, easily reducible to an orthosilicate, $(M\mathit{al}^3)SiO^4$. The formulæ of these minerals are in fact:

$$\begin{array}{ll} \text{Hauyne:} & {}^{3}_{\text{or }4}\Big\}\, M\mathit{al}^3SiO^4 \;.\; Ca^2SO^4 \\ \text{Sodalite:} & 3M\mathit{al}^3SiO^4 \;.\; NaCl \\ \text{Nosean:} & 6M\mathit{al}^3SiO^4 \;.\; Na^2SO^4 \\ \text{Ittnerite:} & 6M\mathit{al}^3SiO^4 \;.\; (Ca^2SO^4;\, NaCl) + 6H^2O \end{array}$$

Hauyne from Niedermendig contains, according to Whitney, 33·90 SiO^2; 12·01 SO^3; 28·07 Al^4O^6; 7·50 Ca^2O and 19·28 Na^2O = 100·73, and is composed of 1 molecule of nosean and 2 molecules of the Albano hauyne. The blue colour of hauyne appears to arise from a small quantity of a metallic sulphide similar to that which gives the colour to ultramarine. All specimens of hauyne, when treated with hydrochloric acid, give off at least a trace of sulphydric acid. (Dana, ii. 230; Handw. d. Chem. iii. 832.)

HAUYNOPHYR. A name applied to the lava of Melfi on the Vulturo. This lava is black or brown, and contains hauyne of various colours, and augite in slender needles. It is strongly attacked by acids. When it is treated with an equal weight of a mixture of 2 pts. hydrochloric acid and 1 pt. water, 30·2 per cent. remains undecomposed, consisting mainly of augite containing a large proportion of iron. The hauyne amounts to 22 per cent. (Rammelsberg, Jahresb. 1860, p. 807.)

HAYDENITE. Yellowish chabasite, from Jones's Falls, Maryland. (See CHABASITE.)

HAYESINE. (Syn. with BOROCALCITE.)

HAYTORITE. Pseudomorphous quartz, from the mine of magnetic iron at Hay Tor, in Devonshire. It has the form of datholite, and contains 98·5 per cent. silica and 0·2 ferric oxide.

HEAT. The word Heat is used in common language, both as the name of a particular kind of sensation, and to denote that condition of matter in which it is capable of producing this sensation in us. Any influence whereby external objects are rendered *hot*, or capable of exciting the sensation of heat, causes them at the same time to undergo other changes, which, being independent of the varying condition of our bodies, afford much more certain and more exact indications as to the condition of heat than is furnished by the sense of touch. Indeed, strictly speaking, our sensations bear no direct testimony with regard to the absolute degree of hotness of external objects, but rather to the fact of their imparting heat to our bodies, or removing heat from them. When these effects are produced in a moderate degree, we experience the sensations of heat and cold respectively; when the loss or gain of heat by our bodies is more rapid, it no longer produces any sensation to which a definite name can be assigned, but simply a feeling of pain; and the very rapid passage of heat either into or out of our bodies, causes a wound which is of the same kind in either case. The direct evidence of our senses with respect to the heat of external objects is therefore confined within comparatively narrow limits. Moreover, it is not always of the same kind, even with respect to bodies in the same condition, as is easily proved by putting one hand into hot water and the other into cold water, and after a short time removing both and plunging them into lukewarm water, which will then feel cold to the hand which was previously in hot water, but warm to the other.

The most important of the other properties of the condition of matter constituting heat, besides producing the sensation denoted by the same word, are the following:

1. Heat imparted to any body raises its *temperature*, that is, it not only causes the body to produce the sensation of heat in a more marked degree, but its tendency to impart the property of so doing—in other words, its tendency to impart heat—to other bodies is increased.

2. It modifies the relations between the density and elasticity of substances, the general law being, that the hotter a body is, the less is its *elasticity of figure*, or tendency to preserve a definite form and arrangement of parts, and the greater is its *elasticity of volume*, or tendency, if solid or liquid, to preserve a definite volume, and if gaseous to expand indefinitely.

3. Heat causes solid bodies to become liquid, and liquid bodies to become gaseous. The amount of heat required to produce these changes in any body varies with its special nature and with other circumstances, but they take place always and without exception, in the same order; that is, the solid state always corresponds to the lowest degree of heat, the gaseous state to the highest degree, and the liquid state to an intermediate degree.

4. Heat causes changes in the chemical composition of bodies, and also in their electrical, magnetic, and optical properties.

The capacity of heat thus to effect changes characterises it as a form of energy, capable of being measured and expressed as a quantity, in terms of one or other of the directly measurable effects which it produces. When thus expressed as a quantity, the condition of heat is found to be subject, like other forms of energy (mechanical energy, for example), to a law of conservation; that is, if in any system of bodies, no heat is expended or produced through changes other than changes of temperature, then the total quantity of heat in the system cannot be changed by the mutual actions of the bodies, but what one loses another gains; and if there are changes other than changes of temperature, then if by those changes the total heat of the system is changed in amount, that change is compensated exactly by an opposite change in some other form of energy. (See Rankine, *A Manual of the Steam Engine and other Prime Movers*, ed. 1861, § 196, pp. 224, 225.)

Hence it follows that heat may be produced by the reversal of its effects: as, for instance, by the conversion of a liquid body into a solid, or of a gas into a liquid; by the compression of a gas, so as to make it occupy a smaller bulk; by the transmission, through the point of junction of two dissimilar metals, of an electric current opposite in direction to that which would be produced by the application of heat at the same point; by the union of oxygen and hydrogen so as to form water, the effect of heat upon water being to resolve it into oxygen and hydrogen gases, &c. &c.

Similarly, heat may be caused to disappear—in other words, cold may be produced—when a change, such as heat is capable of producing, is brought about by other means: as when a solid is liquefied by solution, or when a liquid is vaporised; when a gas is expanded; when, through the point of junction of two dissimilar metals, an electric current is transmitted in the same direction as that which would be produced by the application of heat at the same point, &c. &c.

The reversal of any of its effects does not, however, necessarily and under all circumstances, cause heat to be produced: instead of it an equivalent of some other form of energy may be generated; thus, in Grove's gas-battery (ELECTRICITY, ii. 430) the primary result of the combination of oxygen and hydrogen gases is not the evolution of the quantity of heat which would be required to decompose the water formed, but of an equivalent amount of electrical energy. Neither is the disappearance of heat always a necessary consequence of the production, by other means, of changes such as might be brought about by the action of heat itself: for example, in the decomposition of water by the electric current, there is no disappearance of heat, but there is expended an amount of electrical energy, equivalent to the heat which would otherwise have been required to effect the same decomposition. Further, the most familiar and most practically important processes by which heat is produced, such as combustion, friction, and percussion, are not such as can be directly reversed by the action of heat.

On the other hand, heat being a form of energy, every source or store of energy may be considered as, directly or indirectly, a source of heat. The sources of heat available to man may therefore be classified as follows:

1. The *Sun*. According to Pouillet, the total heating effect of the sun's rays falling perpendicularly during 1 minute upon one square centimetre of the earth's surface, including the portion absorbed by the atmosphere, amounts to 1·7633 times the quan-

tity of heat required to raise the temperature of 1 grm. of water 1 degree centigrade, or to 1·7633 gramme-degrees. The mean heating effect on each square centimetre of the earth's surface, for every minute during 24 hours, is therefore = 0·4408 gramme-degree; or the total effect during one year is 232,000 gramme-degrees.* According to these data, the whole quantity of heat received by the earth from the sun in one year would be sufficient to melt a layer of ice over the whole surface of the earth of 32 metres (or 35 yards) in thickness. The whole of this supply of heat (which is less than the 2,300 millionth part of the total heat emitted by the sun) is not, however, directly available as such. According to Pouillet, nearly one-half is absorbed by the atmosphere, and of the heat so absorbed a considerable proportion goes to supply the mechanical energy of air in motion, or wind, and thus ceases, at least for a time, to exist as heat. Another portion is expended in causing the evaporation of water from the ocean and from the moist surface of the land: as will be shown in the sequel, a great part of this heat reappears when the evaporated water is returned to the earth as rain or otherwise; but the remainder is retained in a modified form in water which is deposited at a higher level than that from which it was evaporated, and so furnishes the mechanical energy, or water-power, of rivers and falling water. Still another portion of the total energy of the sun's rays is absorbed by growing plants, enabling them to convert carbonic acid and water into woody fibre: our ordinary modes of obtaining artificial heat—namely, by the combustion of wood and coal—are processes in which the heat thus absorbed is liberated by the reversal of the chemical changes which take place in plants while living. The warmth and mechanical force of animals are also derived, through the vegetable food which they consume, from the same source, whence are likewise derived, directly or indirectly, our chief supplies of electrical energy.

2. The *internal heat* of the earth. This we may consider as of two kinds: the actual heat, of which there is evidence in hot springs and volcanoes, as well as in the comparatively high temperature of deep mines; and the potential heat stored up in combustible minerals. By far the most important store of potential heat, namely, coal, represents, as we have already seen, a portion of the energy of the sun's rays which reached the earth during the growth of the plants from which it has been formed.

3. The *tidal wave*, caused by the earth's diurnal rotation, combined with the mutual motions of the earth, moon, and sun, is a source of heat which might be rendered practically available, by causing water-wheels, driven by the tidal waters, to generate heat by friction.

4. The *fall of meteoric stones* is a source of heat, practically insignificant, so far as the earth is concerned, but which has been supposed to play an important part in the maintenance of the heat of the sun.

(On the possible sources of energy available to man, see W. Thomson, Phil. Mag. [4] iv. 259.)

On the Measurement of Heat.

Before we can proceed further in the study of the properties and effects of heat, it is necessary that we should have some means of measuring and comparing different quantities of it. As already stated, quantities of heat may be expressed in terms of any of its directly measurable effects; but that one which is usually the most easily and accurately observable is alteration of temperature, and hence quantities of heat are commonly defined by stating the extent to which they are capable of altering the temperature of a known weight (such as 1 grm.) of a known substance (for instance, water). Accordingly, the unit of heat which will be employed in this article is the quantity, already spoken of as a gramme-degree, which is required to raise the temperature of 1 gramme of water from 0° to 1° centigrade. Heat is, however, capable of causing other alterations in the condition of bodies, such as the liquefaction of solid substances, without at the same time causing any alteration in their temperature; hence, another way in which a quantity of heat may be defined is by stating the amount of some known solid (ice, for example) which it is capable of liquefying, without causing any change in its temperature. Quantities of heat can also be expressed in terms of the mechanical or electrical energy to which they are equivalent; but as neither motion nor electricity can be generated by heat without the simultaneous expenditure of a greater or less quantity in causing a rise of

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* The total quantity of heat received in a minute by a hemisphere of the earth's surface is the same as that which would fall on the great circle forming the projection of that hemisphere—that is to say, $1·7633\,\pi R^2$ gramme-degrees (the radius being measured in centimetres). Hence, supposing the heat to be uniformly distributed over this surface, the quantity received in a minute by each square centimetre of surface is

$$\frac{1·7633\,\pi R^2}{4\,\pi R^2} = 0·4408 \text{ gramme-degrees;}$$

and as the earth performs its rotation in 24 hours and the year contains 365 days, it follows that the mean amount of heat received in a year by each square centimetre of the earth's surface is 0·4108 × 60 × 24 × 365, or in round numbers, 232,000 gramme-degrees.

temperature in material substances, and since, therefore, the whole of a given quantity can never be transformed without loss into these other forms of energy, they cannot serve for the direct measurement of heat. And in fact, whatever mode of measurement is adopted, it is always necessary to take account of the temperature of the bodies whose heat is to be estimated, and of those which are influenced by them, in order that we may know the extent to which their temperature is altered; or on the other hand, that we may convince ourselves that no such alteration takes place. The measurement of temperature, or *thermometry*, is therefore a necessary preliminary to the measurement of heat, or *calorimetry*.

Thermometry.—Temperature, or hotness, has already been defined as the tendency of one portion of matter to part with heat to other portions, and has been stated to depend on the quantity of heat which the portion of matter in question contains. For the purpose of defining different temperatures, it is obviously necessary to adopt two standard points, separated by a known and constant interval, which may serve as a measure by which to estimate the interval between any other two temperatures. The standard points usually adopted are the temperature of melting ice, and the temperature of pure water boiling freely under a barometric pressure of 760 millimetres (= 29·92 inches) of mercury (measured at the melting point of ice). When a quantity of mercury is allowed to attain equilibrium of temperature with melting ice, and afterwards with water boiling under the conditions above mentioned, it is found that its bulk in the latter case always exceeds its bulk in the former case by a certain constant amount. The expansion of the mercury is here a measure of the quantity of heat which the boiling water imparted to it after it had come to such a condition that an interchange of heat no longer took place between it and the melting ice; and since, as already observed, the mercury always expands by the same proportion of its bulk at the temperature of melting ice, we may conclude that the quantity of heat which boiling water can impart to a given mass of matter, exceeds that which melting ice can impart to the same mass, by a constant proportion; in other words, that the temperature of boiling water is higher than the temperature of melting ice, and that the interval which separates them is always the same.

It is upon this principle that the use of the mercurial thermometer, and of other instruments in which expansion is employed to indicate temperature, depends. The construction and use of this instrument in its various forms are fully described in the article THERMOMETER, to which the reader is referred. It will be sufficient here to state, that there are in frequent use three different modes of designating the two standard points of temperature, and of subdividing the interval between them: namely, the *centigrade* scale of Celsius employed in this Dictionary, in which the temperature of melting ice is denoted by zero, and the temperature of boiling water by 100; Réaumur's scale, in which the temperature of melting ice is likewise denoted by zero, but that of boiling water by 80; and Fahrenheit's scale, in which the former temperature is marked 32, and the latter 212. The melting point of ice is therefore indicated by any of the following expressions:—

0° C., 0° R., and 32° F.;

and the boiling point of water by any of the following:—

100° C., 80° R., and 212° F.;

accordingly, 100 degrees centigrade are equivalent to 80 degrees Réaumur, and to 180 (= 212 – 32) degrees Fahrenheit, or 5 degrees C. = 4 degrees R. = 9 degrees F. The simplicity of these relations makes it easy, when a temperature is expressed according to any of the three scales, to find an equivalent expression according to either of the other two. (See further the article THERMOMETER.)

Besides the mercurial thermometer, and the spirit thermometer, which is quite similar to it in principle and in the manner in which it is used, there are some other instruments, which are advantageously employed in special cases, for the measurement of temperature, and must therefore be briefly described here.

The *Weight-thermometer*.—This is a mercurial thermometer which differs from the common one, inasmuch as the expansion of the mercury consequent upon rise of temperature is not read off directly from a divided scale, but is calculated from the weight of mercury which escapes from the instrument. It consists of a cylindrical glass reservoir, closed at one end, and terminated at the other by a short capillary glass tube which is so bent that, when the thermometer is placed in the position in which it is to be used, its open end points vertically downwards. The mode of using it is as follows: The thermometer is weighed while empty, and the reservoir and tube are then completely filled with pure mercury, the whole of the air being carefully expelled by boiling, and allowing the instrument to cool while the open end of the capillary tube dips under the surface of mercury, as in the usual process of filling a barometer or thermometer.

By surrounding the thermometer with melting ice, the instrument itself, as well as the mercury contained in it, is brought to the temperature of 0° C.: when this temperature has been reached by every part of it, the vessel of mercury is removed from under the open end of the capillary tube, and is replaced by a small tared capsule. The ice is now removed, and the outside of the thermometer is carefully dried. As the mercury contained in it returns to the temperature of the air (supposed above 0° C.), it expands, and, consequently, some of it escapes by the capillary tube into the tared capsule. The thermometer, and the capsule containing the mercury which has escaped from it, are now placed together in the balance and weighed; by deducting from the gross weight so obtained the weight of the instrument when empty, and that of the capsule, we obtain the weight W, of the quantity of mercury which fills the thermometer at 0° C.

The instrument is next heated to 100° C., by immersing it in the steam of boiling water, the same precautions being taken as in fixing the boiling point of the ordinary graduated thermometer (see THERMOMETER), and the mercury which escapes is collected in the tared capsule and weighed. Let w be the weight of the whole quantity of mercury which escapes from the thermometer when it is heated from 0° C. to 100° C.; then the coefficient of apparent expansion (see below, *Expansion of Liquids*) of the mercury contained in the thermometer will be

$$\delta = \frac{w}{(W - w)100} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Similarly, if w_t be the weight of mercury which escapes from the thermometer when it is heated to any other temperature, t°, which it is required to determine, we have

$$\delta = \frac{w_t}{(W - w_t)t}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

hence we get

$$\frac{w_t}{(W - w_t)t} = \frac{w}{(W - w)100},$$

or—

$$t = \frac{w_t}{w} \cdot \frac{W - w}{W - w_t} \times 100$$

The value of δ, deducible from equation (a), was found by Dulong and Petit (who were the first to employ the weight-thermometer) to be equal to $\frac{1}{6480}$, and by substituting this value in equation (b) the value of t is given independently of the preliminary experiment above described, in which the thermometer is heated to 100° C.; but some uncertainty is thus introduced into the determination, inasmuch as the value of δ varies to a slight extent with the kind of glass of which the thermometer is made.

The weight-thermometer is capable of giving very accurate results when employed to indicate the mean temperature of any considerable space, such as an oil- or water-bath, the temperature of which changes so slowly that it may be assumed, at any given instant, to be the same as that of the thermometer. The size of the instrument depends upon the purpose for which it is to be employed: it is well that it should be of such a length as to reach from one end to the other of the space whose temperature has to be measured, and its capacity ought to be such that the weight of mercury driven out by the smallest rise of temperature which it is required to estimate may be capable of being accurately determined by the balance. An obvious precaution in the use of this instrument is to keep the open end constantly under the surface of the mercury in the capsule, so that no air can enter in consequence of a diminution of temperature.

Regnault's *Air-thermometer* is an instrument which is applicable in the same kind of cases as the weight-thermometer, but has the advantage of giving accurate results at all temperatures below that at which glass softens, whereas the indications of the weight-thermometer are obviously confined to temperatures below the boiling-point of mercury. In construction, it closely resembles the latter instrument, and consists of a cylindrical glass reservoir about 2 centimetres (0·8 inch) in diameter and about 12 or 15 centimetres (5·2 or 6 inches) long, terminated at one end by a narrow glass tube of 1 or 2 millimetres internal diameter, which is bent at a right angle, at a short distance from the end farthest from the reservoir, and drawn out to a fine point. In this state, the instrument is placed in the space of which it is desired to know the temperature; and as soon as the instant arrives for which this temperature is required, the drawn-out point is sealed by fusion with the blowpipe, the height of the barometer and its attached thermometer (i. 512) being observed at the same time. The thermometer thus closed is then supported in a vertical position, the narrow tube downwards, and with the bent and sealed extremity of the latter under the surface of mercury; it is next opened by breaking off, under the mercury, as small a piece as possible of the point; and the reservoir is completely surrounded with melting ice. Owing to the contraction of the air in the thermometer as it cools, the mercury rises in the tube and partially fills the reservoir; and, when the temperature of the thermometer and its contents has been reduced to 0° C., the height of the surface of the mercury in the reservoir, above that of the mercury outside the instrument, is measured by a cathetometer, the height of the barometer being carefully noted at the same time. The open end of the tube is now closed, while still under mercury, by pressing against it a pellet of soft wax; the ice is removed from the reservoir; and the instrument is taken out of the support, inverted, and weighed together with the mercury contained in it. The thermometer is next completely filled with mercury and weighed again, and lastly the weight of the instrument itself when empty is determined.

Let W be the weight of mercury which completely fills the thermometer, and let w be the difference between this weight and that of the mercury contained in it at the first weighing. These two weights then bear to each other the same proportion as the total capacity of the thermometer, at the temperature of the mercury with which it was filled, bears to the volume occupied—at 0° C., and under the atmospheric pressure diminished by the column of mercury read off by the cathetometer—by the air which the thermometer contained at the moment when it was sealed with the blowpipe. They may therefore be taken to represent respectively these volumes: we shall then have

$$W(1 + \kappa t) = w\frac{h}{H}(1 + \alpha t),$$

$$\text{or } t = \frac{W - w\dfrac{h}{H}}{w\dfrac{h}{H}\alpha - W\kappa};$$

where t is the temperature required, expressed in centigrade degrees;

H, the atmospheric pressure at the moment of sealing the thermometer with the blowpipe;

h, the pressure supported by the air in the thermometer at the moment of closing it with the pellet of wax = the barometric pressure observed at the same moment − the column of mercury read off with the cathetometer;

α, the coefficient of expansion of air for 1° C = 0·00366;

κ, the coefficient of cubical expansion of the glass of which the thermometer is made = 0·0000305, between 0° and 300° C., for common glass, and = 0·0000233 for crystal-glass from Choisy-le-Roi. (**Regnault.**)

(For the derivation of the above formula, see the section **Expansion of Gases** in this article; for further details of the air-thermometer, see **Regnault**, *Cours élémentaire de Chimie*, éd. 1854, iv. 64.)

Deville and Troost's *Iodine-pyrometer.*—For the measurement of temperatures above that at which glass softens, Deville and Troost employ a method which depends on essentially the same principles as the use of the air-thermometer, although the mode of experimenting differs considerably. Their apparatus consists of a globular flask of Bayeux porcelain of 280 or 300 c. c. capacity, with a neck 11 centimetres long and 4 mm. in internal diameter. A quantity of iodine is put into the flask, and the neck is nearly closed by a small plug of porcelain which lies loosely in the opening. When the flask is now exposed to a high temperature, the iodine is vaporised and the greater part escapes by the neck, driving out at the same time nearly the whole of the air. After the flask has been exposed for about twenty minutes to the temperature that is to be measured, the flame of an oxy-hydrogen blowpipe is allowed to play for an instant upon the porcelain plug lying in the neck: the plug is thus melted and closes the flask hermetically. When cold, the flask is cleaned and carefully weighed; the end of the neck is broken under boiled water or mercury, and the flask is weighed, together with the water or mercury which enters; it is then completely filled with water or mercury and weighed again; lastly, the flask is weighed when empty. From the weights thus obtained it is easy to calculate the capacity of the flask, and the volume of air which the iodine-vapour has failed to expel: the first weighing gives directly the excess of the weight of the flask and iodine-vapour over that of the empty flask. The observations which require to be made in each experiment are the following:—

Temperature of the balance . . . . = t°
Atmospheric pressure . . . . = h mm.
Excess of weight of flask after being heated and sealed full of iodine-vapour over weight of flask filled with air previous to the experiment . . . . = i grm.
Capacity of flask . . . . = v c. c.
Residual air . . . . = a c. c.

Besides these data, the following constants are required in order to calculate the temperature at which the flask was sealed:—

Weight of 1 c. c. air at 0° and 760 mm. pressure . . . = 0·001293 grm.
Density of iodine-vapour referred to air as unity . . . . = 8·716
Coefficient of expansion of air for 1° C. . . . . . 0·00366
Coefficient of cubical expansion of Bayeux porcelain for 1° C. = 0·0000108

The required temperature, T, can now be calculated as follows:

let $I_w \left(= \frac{(v-a)\cdot001293}{1+\cdot00366t}\cdot\frac{h}{760} + i \right)$ be the total weight of iodine-vapour contained in the flask at the moment of sealing, then

$$\frac{I_w}{0\cdot001293 \times 8\cdot716} \cdot \frac{(1 + 0\cdot00366\ T)\ 760}{h} = I_v$$

will be the volume of this vapour at the same moment; but

$$I_v + \frac{a\,(1 + 0\cdot00366\,T)}{1 + 0\cdot00366t} \cdot \frac{760}{h} = v\,(1 + 0\cdot0000108\ T)$$

and from this equation, in which T is the only unknown quantity, its value is easily found.

It is obvious that this method is applicable only for the measurement of maximum temperatures which can be maintained stationary for some time; but in cases where these conditions can be fulfilled, as in determining the boiling points of difficulty volatile substances (*e.g.* sulphur, cadmium, zinc) it is capable of yielding very accurate results.

A porcelain globe filled with air may be employed as a thermometer in the same way: the advantage of using iodine is that given differences of temperature correspond to greater differences of weight.

(See further Deville and Troost, Ann. Ch. Phys. [3] lviii. 267, 275, 285, 293.)

Mercury-pyrometer.—This instrument, proposed by Regnault (Ann. Ch. Phys. [3] lxiii. 40), is composed of a bottle made of cast or wrought iron, platinum or porcelain, having a capacity of 500 to 1000 c. c., and provided with a perforated lid which lies flat upon the neck of the bottle, the under surface of the lid (which has a considerably greater diameter than the neck) and the upper surface of the neck being ground together, so that by sliding the lid a little to one side, the bottle can be almost completely closed without removing it from the furnace, or other space whose temperature is to be determined. Before beginning the experiment, 10 or 15 grms. of pure mercury are put into the bottle, and it is then placed in the furnace, the lid being laid on so that the hole through it forms a continuation of the orifice of the neck; when the bottle has been in the furnace long enough to have thoroughly assumed the temperature of the latter, it is closed by drawing the lid sideways, then removed from the furnace, and quickly cooled. The mercury remaining in the bottle is poured out (it can be completely detached from the bottle by shaking a little water round in it), and weighed, either in the metallic state, or, when necessary, after solution in an acid and precipitation. When the following data are known, namely—

v = capacity of the bottle in c. c. at 0° C.;
κ = coefficient of cubic expansion of the substance of the bottle;
h = atmospheric pressure at the moment of withdrawing the bottle from the furnace;
d = density of mercury-vapour at temperatures at which it has the properties of a perfect gas;
p = weight of mercury remaining in the bottle;

the required temperature, T, can be calculated.

The weight of mercury-vapour which fills the bottle at T° is

$$= v \cdot \frac{1 + \kappa T}{1 + 0\cdot00366\,T} \cdot 0\cdot0012932 \,.\, d \,.\, \frac{h}{760} = p;$$

hence

$$\frac{1 + \kappa T}{1 + 0\cdot00366\ T} = \frac{760}{v\ \ 0\cdot0012932 \,.\, d} \cdot \frac{p}{h} = M \cdot \frac{p}{h},$$

in which last expression M is a quantity which remains constant for the same bottle: we have therefore

$$T = \frac{1 - M\,\frac{p}{h}}{M \,.\, 0\cdot00366\ \frac{p}{h} - \kappa}$$

Regnault's *Hydrogen-pyrometer* (Ann. Ch. Phys. [3] lxiii. 42) is an instrument whereby the temperature of a furnace or other heated space can be quickly determined at any required instant. It consists of a wrought iron tube one or two inches wide, and long enough to reach from one side of the furnace to the other, terminated at each end by a capillary tube of the same material, provided with a three-way cock. When the temperature of the furnace is to be determined, a current of pure and dry hydrogen is caused to enter the iron tube at one end, and allowed to issue freely into the air at the other; when the current of gas has been continued long enough to displace all the air, and to reduce any oxide that may have formed in the inside of the tube, it is stopped; the free end of the iron tube is connected with a copper tube filled with oxide of copper, and heated to redness by a row of gas-jets; the current of hydrogen is then replaced by a slow current of dry air, which sweeps forward the hydrogen into the copper tube, where it is completely converted into water. The water thus formed passes on to a weighed U-tube containing pumice-stone and sulphuric acid, and from its weight the temperature of the furnace can be calculated upon the same principle as when the mercury pyrometer is used. (For further details, and for figures of this apparatus and of that last described, see Regnault, *loc. cit.*)

The *Thermomultiplier*.—This instrument consists of a thermo-electric pile, connected with a delicate galvanometer; its construction, and the principles upon which its action depends, have already been explained in the article ELECTRICITY (ii. 413 and 443, 444). As a thermoscope, or instrument for rendering sensible heat of very low intensity, this apparatus is much more delicate than any other that has been devised, the heat given out by the human body producing a perceptible effect upon it, even at a distance of ten yards or more (Daguin, *Traité de Physique*, 2nd edit. ii. 34). As a differential thermometer, it is capable of giving accurate results, when the intervals of temperature to be measured are sufficiently small. But, since the direct indications of the instrument are not generally proportional to these intervals of temperature, it is necessary to construct, for each thermomultiplier, a table showing the interval of temperature to which each degree read off upon the instrument really corresponds. The following account of the method recommended by Melloni for constructing these tables is given by Tyndall (*Heat as a Mode of Motion*, p. 355), being translated by him from 'La Thermocrose,' p. 59:—

"Two small vessels are half-filled with mercury, and connected separately by two short wires, with the extremities of the galvanometer. The vessels and wires thus disposed make no change in the action of the instrument; the thermo-electric current being freely transmitted, as before, from the pile to the galvanometer. But if, by means of a wire, a communication be established between the two vessels, part of the current will pass through this wire and return to the pile. The quantity of electricity circulating in the galvanometer will be thus diminished, and with it the deflection of the needle.

"Suppose, then, that by this artifice we have reduced the galvanometric deviation to its fourth or fifth part; in other words, supposing that the needle being at 10 or 12 degrees, under the action of a constant source of heat, placed at a fixed distance from the pile, that it descends to 2 or 3 degrees when a portion of the current is diverted by the external wire; I say that by causing the source to act from various distances, and observing in each case the *total* deflection and the *reduced* deflection, we have all the data necessary to determine the ratio of the deflections of the needle, to the forces which produce these deflections.

"To render the exposition clearer, and to furnish, at the same time, an example of the mode of operation, I will take the numbers relating to the application of this method to one of my thermomultipliers.

"The external circuit being interrupted, and the source of heat being sufficiently distant from the pile to give a deflection not exceeding 5 degrees of the galvanometer, let the wire be placed so as to connect the two vessels of mercury; the needle falls to 1·5. The connection between the two vessels being again interrupted, let the source be brought near enough to obtain successively the deflections:—

5°, 10°, 15°, 20°, 25°, 30°, 35°, 40°, 45°.

Interposing after each the same wire, we obtain the following numbers:—

1·5°, 3°, 4·5°, 6·3°, 8·4°, 11·2°, 15·3°, 22·4°, 29·7°.

"Assuming the force necessary to cause the needle to describe each of the first degrees of the galvanometer to be equal to unity, we have the number 5 as the expression of the force corresponding to the first observation. The other forces are easily obtained by the proportion:—

$$1{\cdot}5 : 5 = a : x = \frac{5}{1{\cdot}5}\,a = 3{\cdot}333a,$$[*]

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[*] That is to say, one reduced current is to the total current to which it corresponds, as any other reduced current is to its corresponding total current.

where *a* represents the deflection when the exterior circuit is closed. We thus obtain

5, 10, 15·2, 21, 28, 37·3

for the forces corresponding to the deflections,

5°, 10°, 15°, 20°, 25°, 30°.

"In this instrument, therefore, the forces are sensibly proportional to the arcs up to nearly 15 degrees. Beyond this the proportionality ceases, and the divergence augments as the arcs increase in size.

"The forces belonging to the intermediate degrees are obtained with great ease, either by calculation or by graphical construction, which latter is sufficiently accurate for these determinations.

"By these means we find,

Degrees . .	13°	14°	15°	16°	17°	18°	19°	20°	21°
Forces . . .	13	14·1	15·2	16·3	17·4	18·6	19·8	21	22·3
Differences . .	1·1	1·1	1·1	1·1	1·2	1·2	1·2	1·3	
Degrees . .	22°	23°	24°	25°	26°	27°	28°	29°	30°
Forces . . .	23·5	24·9	26·4	28	29·7	31·5	33·4	35·3	37·3
Differences . .	1·4	1·5	1·6	1·7	1·8	1·9	1·9	2	

"In this table we do not take into account any of the degrees preceding the 13th, because the force corresponding to each of them possesses the same value as the deflection.

"The forces corresponding to the first thirty degrees being known, nothing is easier than to determine the values of the forces corresponding to 35, 40, 45 degrees, and upwards.

"The reduced deflections of these three arcs are,

15·3° 22·4°, 29·7°.

"Let us consider them separately; commencing with the first. In the first place, then, 15 degrees according to our calculation, are equal to 15·2; we obtain the value of the decimal 0·3 by multiplying this fraction by the difference 1·1; for we have evidently the proportion

$$1 : 1·1 = 0·3 : x = 0·3$$

The value of the reduced deflection corresponding to the 35th degree, will not, therefore, be 15·3°, but 15·2° + 0·3° = 15·5°. By similar considerations we find 23·5° + 0·6° = 24·1°, instead of 22·4°, and 36·7° instead of 29·7° for the reduced deflections of 40 and 45 degrees.

"It now only remains to calculate the forces belonging to these three deflections, 15·5° 24·1°, and 36·7°, by means of the expression 3·333*a*; this gives us,

the forces, 51·7, 80·3, 122·3.
for the degrees, 35, 40, 45.

"Comparing these numbers with those of the preceding table, we see that the sensitiveness of our galvanometer diminishes considerably when we use deflections greater than 30 degrees."

When one face of the thermopile is exposed to the action of heat, the needle of the galvanometer, with which the pile is connected, immediately leaves its position of equilibrium and swings considerably beyond the new position in which, after a series of gradually diminishing oscillations, it ultimately comes to rest, if the pile continues exposed to the same source of heat; and when the source of heat is removed, the face of the pile only gradually loses the increased temperature which it had acquired while exposed to its action, so that the return of the galvanometer needle to its first position is likewise gradual. These two circumstances would occasion a very considerable loss of time in making a numerous series of observations with the thermomultiplier, were it necessary each time to allow the needle to become stationary at the point of ultimate deflection; but Melloni observed that the arc through which the needle swings in its first oscillation is always the same for an ultimate deflection of the same amount, and hence, by constructing what he calls a *Table of Impulses*, or table giving the ultimate deflection corresponding to a first swing, or impulse, of any given amount, this loss of time may be avoided. With such a table, it is only necessary to observe the arc described by the needle in its first movement, and then to refer to the table for the ultimate deflection corresponding thereto.

Siemens's *Resistance Thermometer*.—In this instrument the actual indications of temperature are made by an ordinary mercurial thermometer: its peculiarity consists in the fact that it enables the temperatures of spaces to be determined into which a thermometer could not be introduced, or where, if introduced, it could not be observed. Its action depends on the increased resistance which a metallic wire offers to the passage of an electric current when its temperature is raised. (ELECTRICITY, ii. 467.)

Two perfectly similar coils of insulated wire are enclosed in two hermetically sealed copper cases. One is placed in the space of which the temperature is required, the other in a bath of water; and the temperature of the bath is altered until the electrical resistance of the two coils is exactly equal, an equality which can be readily tested by a differential galvanometer. The temperature of the bath will then clearly be equal to that of the space where the first resistance coil is placed. The connections are made with very thick copper wire, so that their resistance shall have little or no influence upon the result. The wires are coiled on an open copper cylinder of considerable diameter and length, so as to expose a large surface to the air or water in which they are placed. They in consequence take the temperature of the surrounding medium with great rapidity. (*Report on Electrical Instruments in the International Exhibition of* 1862, by Fleeming Jenkin.—Jurors' Reports, Class xiii. p. 93.)

This instrument is obviously adapted for determining the temperature of different depths of the sea, or of borings on land, and for other similar purposes. Its sensibility may be considerably increased by adopting a suggestion of Dr. Esselbach's, and constructing one of the coils, that one which is placed in the bath of water, of a material whose resistance increases more slowly with rise of temperature than that of the substance of which the other coil is made. The temperature of the bath would then have to be varied more than one degree, in order to compensate the alteration of resistance caused by a variation of one degree in the temperature of the medium surrounding the other coil.

Besides the instruments for measuring temperature which are described above and in the article THERMOMETER, already referred to, a great number of others, of various degrees of utility, have been suggested from time to time. But it is believed that the instruments here noticed are those most likely to be found practically useful by the experimental chemist. A large number of the older contrivances for thermometric purposes are very fully described in the treatise on *The Thermometer and Pyrometer*, published by the Society for the Diffusion of Useful Knowledge. (Library of Useful Knowledge, Natural Philosophy, vol. ii. 1832.)

Calorimetry.—The cases in which *quantities* of heat require to be measured are very numerous, and different methods and apparatus are required in nearly every case. In relation to every one of the effects of heat the question arises: How much heat is needed to produce this effect with a given intensity? hence calorimetric measurements have to be made in the study of each of these effects, while the nature of each will determine the manner in which such measurements can best be made. We shall, therefore, consider the different problems into which calorimetry enters, one by one as they occur, and shall now pass at once to the

QUANTITATIVE STUDY OF THE EFFECTS OF HEAT.

The following order will be adopted in this part of the subject:—

1. Changes of Temperature produced by Heat.
2. Changes of Volume produced by Heat.
3. Changes of State of Aggregation produced by Heat.
4. Relations of Heat to Chemical Affinity.
5. Relations of Heat to Electricity.
6. Relations of Heat to Mechanical Energy.

1. *Changes of Temperature produced by Heat.*—**Specific Heat.**—When equal weights of two different substances, say a pound of water and a pound of mercury, are placed in two similar vessels, and exposed for the same length of time to the heat of the same lamp, or placed in front of the same fire, at equal distances from it, or otherwise treated so as to have an opportunity of taking up, each exactly as much heat as the other, it is found that, if of equal temperatures at the beginning of the experiment, they have no longer the same temperature at the end of it. The mercury is found to be much hotter than the water. Hence it is proved that a quantity of heat which is sufficient to raise the temperature of a given quantity of mercury through a given number of degrees, is only able to raise the temperature of the same quantity of water through a smaller number of degrees; in other words, more heat is required to raise the temperature of a given quantity of water one degree, than is required to raise the temperature of the same quantity of mercury one degree. Again, if we take two equal weights of water and mercury which have been heated to the same temperature, say to 100° C., and place them under such conditions that, in cooling down to the temperature of the atmosphere, each shall give out exactly as much heat in each second as the other, it will be found that the mercury will have cooled down to the temperature of the atmosphere long before the water; hence, when its temperature is lowered by a given number of degrees, water gives out more heat than an equal quantity of mercury does in undergoing a similar alteration of temperature. Extending similar experiments to other substances, we should find that the quantity of heat needed to effect a given

change of temperature is different for almost every substance. These quantities of heat, expressed relatively to the quantity of heat required to raise the temperature of an equal weight of water from 0° to 1° C., are called the specific heats of the various substances. Thus, for instance, the statement that the specific heat of lead is 0·0314, implies that the quantity of heat which would suffice to raise the temperature of any given quantity of lead from 0° to 1° C., would raise the temperature of an equal quantity of water only from 0° to 0·0134°.

The power of heat, then, to cause changes of temperature depends upon the nature of the substance upon which it acts, just as we shall see in the sequel, that its power to cause changes of volume, or changes of any other kind, varies with the nature of the bodies submitted to its action.

Three principal methods have been employed for measuring the specific heats of different substances. Of these, much the most accurate is that known as the method of mixtures; we shall, therefore, describe it first. It consists in heating a known weight of the substance, whose specific heat is to be determined, to a known temperature, then plunging into a known weight of water, also at a known temperature, and determining the temperature of the mixture which results. In an experiment of this kind, let T be the temperature to which the substance was heated, t the initial temperature of the water, and θ the temperature of the mixture; and let the weight, in grammes, of the substance be W, and the weight of the water, w. Then it is plain that the heat which the substance has given out in cooling from $T°$ to $\theta°$ is the same as that required to heat the water from $t°$ to $\theta°$. Calling the hitherto unknown specific heat of the substance x, we shall have for the former quantity of heat, the expression $W(T-\theta)x$, and for the heat taken up by the water (whose specific heat $=1$), $w(\theta-t)$. Hence

$$W(T-\theta)x = w(\theta - t);$$

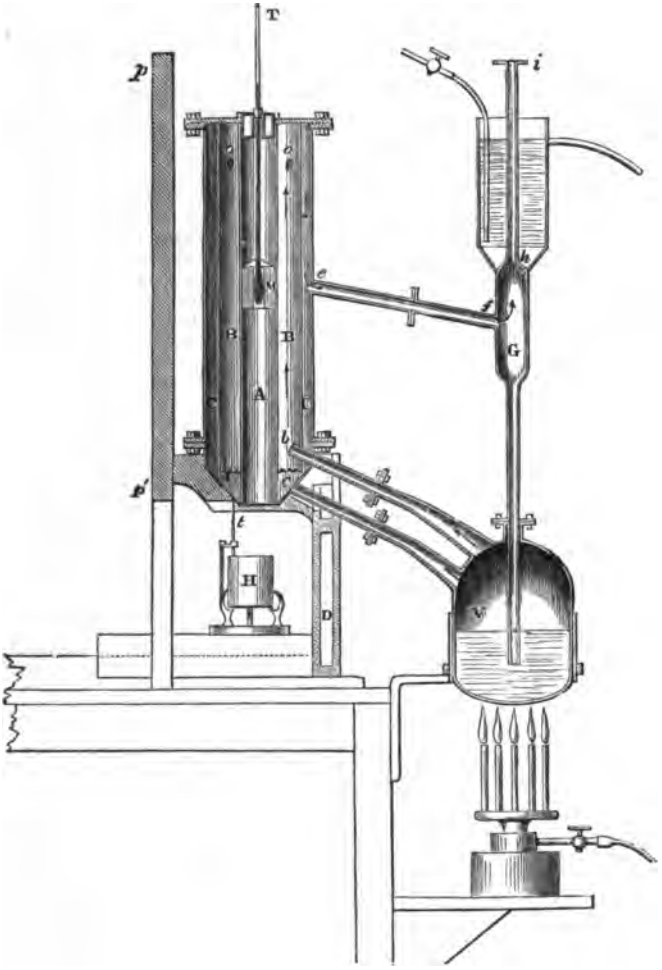
or

$$x = \frac{w(\theta - t)}{W(T-\theta)}.$$

The most accurate determinations of specific heat that have hitherto been published are probably those made by Regnault (Ann. Ch. Phys. lxxiii. 5; *Ibid.* [3] i. 129; ix. 322; xxvi. 261 and 268; xxxviii. 129; xlvi. 257; lxiii. 5), by the method of mixtures. *Fig.* 530 (see p. 26), which is copied from his latest memoir on this subject, shows the disposition of apparatus usually employed by this investigator. The substance to be examined is contained in a basket of fine brass wire, M, suspended in the middle of an upright cylinder, A, of thin metal. This cylinder is surrounded by a larger concentric cylinder, B, and this again by a third cylinder, C. By the ebullition of water in the boiler, V, the annular space between A and B is kept constantly full of steam, which passes thence through the openings, *o o*, near the top of B, into the outer annular space comprised between B and C, and hence by the waste-pipe *ef* to the condenser G, and so back to the boiler. That portion of the steam which is liquefied in the cylinders B and C, returns to the boiler in the form of water by the pipe *c*. The temperature of the substance in M is shown by the thermometer T, the bulb of which occupies a cylindrical space left for the purpose in the middle of the basket of brass wire. The water into which the substance is to be plunged is contained in the calorimeter H, a small vessel of very thin and highly polished brass, supported upon three points, and carried by a foot which slides along a groove, so that, by a rapid and smooth motion, it can be brought directly under A, or removed to the farther side of the sliding screen, *pp'*, so as to be protected from the influence of heat given out by the heating apparatus C. When in its place under A, the calorimeter is protected from heat radiated by the boiler by the double screen D, between the two coatings of which a continual circulation of cold water is kept up. The temperature of the calorimeter is indicated by the thermometer *t*, the bulb of which is long enough to reach from just below the surface of the water to very near the bottom.

At the commencement of an experiment, the calorimeter is drawn back outside the screen *pp'*, and the basket containing the substance to be examined is suspended in the middle of the cylinder A by a silk thread, the cylinder itself being closed at top and bottom by hollow plugs to prevent loss of heat, one of which is shown in its place at the upper part of the figure. Steam from the boiler being allowed to circulate about A, the substance at M is gradually heated to nearly the temperature of boiling water. After, in general, about two hours, the thermometer T becomes stationary; but, for greater certainty that the temperature of the substance is uniform throughout, the heating is continued for at least another hour. The temperature of the water in the calorimeter is then observed by reading the thermometer *t* through a telescope, the temperature of the air being read off at the same time upon another thermometer. The calorimeter is quickly pushed under the heating apparatus; the plug at the bottom of the cylinder A is removed; and by loosening the cork which supports the thermometer T the silk thread from which the basket M hangs is liberated, and this with its contents allowed to fall into the water contained in H. The calorimeter is again drawn back behind the screen PP′, and the basket is moved about in the water by an assistant, while the observer watches through the telescope the maximum temperature indicated by the thermometer *t*. This maximum generally occurs one or two minutes after the immersion of the substance. Suppose that, in such an experiment, the following results were obtained:—

Fig. 520.



Weight of substance	*M* grm.
„ „ brass wire basket	*p* grm.
Temperature by thermometer T at moment of immersion	$T°$
Temperature by thermometer *t* at same moment	$t°$
Maximum temperature after immersion by thermometer *t*	$\theta°$
Weight of water in calorimeter, calorimeter and thermometer supposed included	*A*
Specific heat of brass	*c*

Then, calling the required specific heat of the substance C, we should have

$$MC(T - \theta) + pc(T - \theta) = A(\theta - t);$$

or

$$C = \frac{A(\theta - t)}{M(T - \theta)} - pc(T - \theta).$$

In giving the calculation in this very simple form, we are assuming that the constant A includes not merely the actual water in the calorimeter, but also the "water-equivalents" of the brass of which the calorimeter is composed, and of the glass and mercury composing the thermometer t, for these are all heated at the same time as the water, and to the same extent. If the weight of brass in the calorimeter were w, and the weights of glass and mercury in the thermometer t respectively w' and w'', and if, further, the specific heats of brass, glass, and mercury be c, c', and c'', the "water-equivalent" of the calorimeter (or the quantity of water which would require the same quantity of heat to raise its temperature one degree) would be wc, and the "water-equivalent" of the thermometer t would be $w'c' + w''c''$. Hence if a be the weight of actual water in the calorimeter, the calorimetric value of the whole quantity of matter to which the heat of the body under experiment is imparted will be:

$$A = a + wc + w'c' + w''c''.$$

The values of the several terms making up the whole value of A must obviously be determined by preliminary experiments.

An additional correction, the value of which has also to be found by preliminary trials, is required to compensate the heating or cooling effect of the atmosphere upon the calorimeter and its contents during the course of an experiment. But as the difference between the two temperatures t and θ of the calorimeter seldom exceeds 4° or 5°, it is easy, by keeping the temperature of the instrument as much below the atmospheric temperature during the first half of the experiment as it is expected to exceed it in the second half, to render the error introduced by atmospheric heating or cooling, very small indeed: in Regnault's experiments, it amounted to only three or four hundredths of a degree, but was nevertheless carefully allowed for.

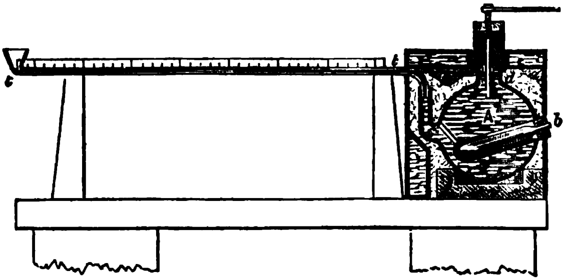
By means of the apparatus above described, the substance under examination can never be heated quite to the boiling point of the liquid in the boiler V, so that when this is water, the temperature of the substance never rises above 97° or 98°; but any other temperature that may be desired can easily be attained by introducing into the boiler, in place of water, a liquid which boils at nearly the required temperature, and then raising or lowering its temperature of ebullition as much as may be needed, by connecting the tube *h i* with a large reservoir of compressed or rarefied air.

In determining the specific heat of substances (such as phosphorus, for example) which could not be heated without causing them to melt or else to undergo other alterations which would interfere with the accuracy of the results, Regnault adopted an inverse process, and cooled them to a temperature considerably below that of the water in the calorimeter, and thus observed the diminution in the temperature of the latter which resulted from immersing the cooled substances in it. The apparatus employed for producing and maintaining constant a low temperature, resembles to some extent the heating apparatus already described and figured. It consists of a central tube, in the middle of which is suspended the substance to be cooled, surrounded by two larger concentric cylinders. The space between the central tube and the next is partially filled with ether or some other volatile liquid, and the space between this tube and the outside one is filled with air. By causing a rapid current of air to traverse the ether, its temperature is gradually lowered, and with an external temperature of 20° C. any temperature not lower than −12° can be maintained constant by properly regulating the flow of air; the lowest temperature that can be obtained under similar circumstances, by employing sulphide of carbon instead of ether is − 8°. By the use of liquid ammonia, any temperature between −40° and −80° C. can be obtained.

In order to apply the above method to determinations of the specific heat of liquids, they must be enclosed in tubes of very thin glass, nearly filled and hermetically closed. These tubes are suspended, like the basket M, in the centre of the tube A, and afterwards let down into the calorimeter. In calculating the result, allowance must of course be made for the heat imparted to the calorimeter by the tube.

Another apparatus which serves for the determination of specific heats is represented in *fig.* 531. This apparatus, devised by Favre and Silbermann (Ann. Ch. Phys. [3] xxxvi. 33), consists of a glass globe, A, of about 1 litre capacity, in which are three openings. The first, *b*, admits a thin iron or platinum tube, closed at the lower end, about 1 inch ($2\frac{1}{2}$ to 3 centimetres) wide and 4 inches (10 or 11 centimetres) long, cemented at the top into the opening of the glass, and kept in its place below by a piece of glass rod, one end of which is cemented against the upper side of the tube and the other end against the side of the glass globe. Within this tube, which is called the *muffle*, is placed another tube of very thin glass which serves to contain the substances under experiment. This is held in its place by a cork which surrounds its neck and fits tightly in the mouth of the muffle; it is surrounded by about 100 grms. of mercury, intended to facilitate interchange of heat between it and the muffle.

Fig. 531.



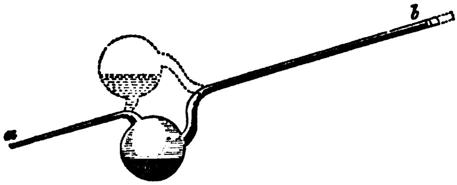
The second opening, *c*, carries a horizontal capillary tube, *tt*, about 500 millimetres long, divided into millimetres, and terminated at the farther end by a small funnel. This tube, which should be perfectly cylindrical, is cemented to the glass globe by marine glue, so that, when needful, it can be easily removed and cleaned.

The third opening carries a steel piston, *d*, which, by means of a screw, can be raised or lowered so as to increase or diminish somewhat the capacity of the globe.

The globe itself is supported upon a thick ring of cork and enclosed in a box lined with wadding or swan's-down, and surrounded by a double casing filled with water. It is filled with mercury, with the precautions necessary to exclude any trace of air, and the extremity of the column of mercury is adjusted by moving the steel piston, *d*, up or down, so as to be exactly at the zero point of the divisions of the tube.

In using the instrument, the substance whose specific heat is to be determined, is introduced at a known temperature into the muffle, or into the glass tube inside it. The substance then parts with its heat to the mercury contained in the globe of the calorimeter, causing it to expand, and the expansion read off on the tube *tt* is a measure of the quantity of heat thus imparted to the mercury. In order, however, to compare the indications of this instrument with those of the water-calorimeter, it is needful to know the number of divisions of the tube *tt* which correspond to the effect of a unit of heat, or gramme-degree. For this purpose Favre and Silbermann graduated their instrument as follows:—A few scraps of platinum wire, and 4 or 5 grammes of distilled water, are placed in a pipette of the form shown in *fig.* 532. The pipette is heated over a spirit-lamp until the water boils, the flame being occasionally passed along the point *a*, so as to heat it sufficiently to prevent the condensation of steam, and the drop of water is removed from the end by a piece of filter-paper, so that the steam may have free issue into the air at the moment of beginning the experiment.

Fig. 532.



The lamp is then removed for an instant; the ebullition ceases, and at the same moment the point of the pipette is rapidly introduced to the bottom of the tube contained in the muffle, the pipette being simultaneously turned round through 180° about the axis *ab*. The lamp is then again brought near the pipette, and the cork which closes the upper end is removed, so that no steam may follow the water into the muffle. As soon as the mercury-column in *tt* has reached the extreme point, the temperature of the water is taken by a small and sensitive thermometer; and the experiment is completed by weighing the glass tube with the water contained in it.

If the weight of water be P, and the number of degrees through which its temperature falls after being introduced into the tube of the muffle be T, the number of units of heat imparted to the calorimeter will be P T. If this quantity of heat causes the mercury to advance through N divisions of the tube *tt*, the amount of expansion, C, expressed in the same divisions, corresponding to one unit of heat will be

$$C = \frac{N}{PT}.$$

Favre and Silbermann found that, in the instrument employed by them, one unit of heat caused the mercury to advance in *tt* by 0·3 millimetre.

In determining the specific heats of liquid substances by means of this apparatus, they are introduced into the tube of the muffle by means of the pipette *ab*, in the manner already described in the case of water, the weight employed being determined after the experiment.

Another method of ascertaining the specific heats of various substances consists in determining the quantity of ice which can be melted by the heat given off by a known weight of each while cooling through the same number of degrees. A known weight of the substance to be operated upon is heated to a determinate temperature, as 100°, and then placed in a cavity scooped out of a block of melting ice and covered by a second slab of ice. The temperature of the substance is thus brought down to that of melting ice, and a quantity of ice is melted—that is, a quantity of water is formed—proportionate to the quantity of heat which the substance gives out in cooling to this temperature.

This method, however, though very simple both in principle and in execution, cannot be made to give very accurate results; for there is great difficulty in determining with exactness the quantity of water formed, and a small error committed here will introduce a large error into the estimate of the quantity of heat given out by the body in cooling, since as will be seen hereafter, the quantity of heat needed to convert one part of ice into water would be sufficient to raise the temperature of 79¼ parts of water one degree.

A third method, called the method of cooling, was employed by Dulong and Petit. It consists in determining the length of time which the different substances to be examined require in order to cool in a vacuum from one known temperature to another, each being placed, as nearly as possible, under identical circumstances.

In order to realise the necessary conditions for determinations of this kind, the substances to be examined are all reduced to an impalpable powder, and filled successively into the same cylindrical silver vessel, gilded and highly polished externally, in the axis of which is the bulb of the thermometer by which the progress of the cooling is to be shown. The silver vessel, supported by the stem of the thermometer, is suspended in the middle of a large brass receiver, coated internally with lamp-black, from which the air can be completely removed. This is immersed in water at 40° C., and when the thermometer inside the apparatus marks 35°, it is transferred to melting ice. The thermometer is now watched through a telescope, and the instants at which it marks 20°, 15°, 10°, and 5°, are noted. If all other circumstances were the same, the time during which each substance underwent the same fall of temperature, would be a measure of the amount of heat given out in undergoing this change—that is, of the specific heat of the substance; but Regnault, who submitted this method to very careful examination (Ann. Ch. Phys. [3] ix. 327), found that it was impossible to obtain results of any value by its application in the case of solid bodies: with liquids, for which the same sources of error do not occur as for solids, it is capable of giving much more exact results.

The difficulties attendant on the exact determination of the specific heats of gases and vapours are very much greater than in the case of solids and liquids. An extensive series of experiments on this subject has been made by Regnault (Mém. de l' Acad. des Sciences, xxvi. 41) with elaborate care, the principle of his method being to observe the alteration of the temperature of water, surrounding a spiral tube, caused by the passage through the tube of a known quantity of gas which enters and issues from it at known temperatures. A description of the apparatus employed in these researches and of the methods of experimenting would occupy too much space to admit of its being given here; we must therefore refer for details to the paper already quoted. (A figure of the apparatus and a tolerably full account of the method of experimenting are also given in Daguin's *Traité de Physique*, 2nd edit. ii. 275–280.) The principal results obtained are enumerated below (p. 35).

In the following Table are given the specific heats of a considerable number of the elementary bodies, according to the results obtained by Regnault by the method of mixtures. When the specific heat of the same element has been determined by him several times, the most recent result is given in the Table. The third column gives the temperatures between which the specific heats given in the second column were observed; the numbers contained in the fourth and fifth columns will be referred to presently. The specific heats of the gaseous elements are not included in this table, but will be found in a subsequent one, together with the specific heats of some other gases (see p. 35).

Table of Specific Heats of the Elements.

Name.	Specific heat.	Temperature.	Atomic weight.	Product of sp. ht. × at. wt
Lithium	0·94080	100° to 27°	7 (=Li)	6·59
Sodium	·29340	6 „ −32	23 (=Na)	6·75
Magnesium	·24990	98 „ 23	24 (=Mg^2)	6·00
Aluminium (sp. heat corrected for 2 p. c. iron impurity)	·21430	97 „ 14	27·5 (=Al^2)	5·89
Phosphorus liquid	·21200	100 „ 50	31 (=P)	6·57
solid	·18870	30 „ −10		5·85
„	·17400	10 „ −78		5·39
amorphous	·17000	98 „ 15		5·27
Sulphur (recently melted)	·20259	98 „ 14	32 (=S)	6·48
Sulphur (native)	·17760	99 „ 14		5·68
Potassium	·16956	0 „ −78	39 (=K)	6·61
Manganese (containing a trace of silicon)	·12170	97 „ 14	55 (=Mn^2)	6·69
Iron	·11380	98 „ 17	56 (=Fe^2)	6·37
Nickel specimen I. (1840)	·10863	99 „ 13	58·7 (=Ni^2)	6·37
„ II. (1859)	·10752	97 „ 17		6·31
„ III. (1859)	·11080	97 „ 12		6·50
Cobalt specimen I. (1840)	·10696	99 „ 12	58·7 (=Co^2)	6·28
„ II. (1859)	·10620	98 „ 10		6·23
„ III. (1859)	·10730	97 „ 8		6·30
Copper	·09515	98 „ 15	63·5 (=Cu^2)	6·04
Zinc	·09555	99 „ 14	65 (=Zn^2)	6·21
Arsenic	·08140	98 „ 13	75 (=As)	6·11
Selenium metallic	·07616	97 „ 21	79 (=Se)	6·02
	·07446	7 „ −18		5·88
vitreous	·10310	82 „ 19		8·15
	·07468	8 „ −24		5·90
Bromine solid	·08432	−20 „ −78	80 (=Br)	6·75
liquid	·11294	58 „ 13		
	·11094	48 „ 10		
	·10513	10 „ − 6		
Molybdenum (impure)	·07218	98 „ 12	96 (=Mo^2)	6·93
Rhodium specimen I.	·05527	98 „ 20	104·4 (=Rh^2)	5·77
„ II.	·05803	97 „ 11		6·07
Palladium	·05928	98 „ 14	106 (=Pd^2)	6·28
Silver	·05701	99 „ 13	108 (=Ag)	6·16
Cadmium (containing 1 per cent. impurity)	·05669	98 „ 16	112 (=Cd^2)	6·35
Tin	·05623	99 „ 12	118 (=Sn)	6·63
Uranium (impure)	·06190	98 „ 10	120 (=U^2)	7·43
Antimony	·05077	97 „ 12	122 (=Sb)	6·19
Iodine	·05412	98 „ 9	127 (=I)	6·87
Tellurium	·04737	98 „ 18	128 (=Te)	6·06
Tungsten	·03342	98 „ 12	184 (=W^2)	6·15
Gold	·03244	98 „ 12	196 (=Au)	6·36
Iridium	·03259	99 „ 17	198 (=Ir^2)	6·45
Platinum	·03243	99 „ 12	198 (=Pt^2)	6·42
Osmium	·03113	98 „ 19	199·2 (=Os^2)	6·20
Mercury solid	·03192	−40 „ −78	200 (=Hg^2)	6·38
liquid	·03332	98 „ 12		6·66
Thallium according to Lamy	·03250		204 (=Th)	6·63
„ Regnault	·03355	100 „ 17		6·84
Lead	03140	98 „ 15	207 (=Pb^2)	6·50
	·03065	10 „ −78		6·35
Bismuth	·03084	98 „ 13	210 (=Bi)	6·48
Boron graphitic	·23520	99 „ 17	11 (=B)	2·59
crystallised	·25000	100 „ 11		2·75
Carbon wood charcoal	·24150	98 „ 8	12 (=C)	2·90
graphite	·20083	98 „ 12		2·41
diamond	·14687	98 „ 9		1·76
Silicon crystallised	·17740	99 „ 12	28 (=Si)	4·97
fused	·17500	100 „ 22		4·90

The following short table gives the specific heats of a few substances which require to be taken into account in calculating the results of the experiments from which the numbers in the foregoing and subsequent tables are deduced:—

Name of Substance.	Specific heat.	Temperatures between which the specific heat was observed.
Brass	0·09391	98° and 12°
Glass	0·19768	99 „ 14
Oil of turpentine	0·42593	98 „ 15
Water	1·00800	98 „ 13

Numerous determinations have been made by Regnault of the specific heats of inorganic compounds. A selection from his results, sufficient to show their general nature, is given in the next table. The temperatures between which the determinations were made are not given in the table, but were in all cases a temperature approaching 100° C., and a temperature near that of the atmosphere. In the case of substances which are soluble in water, or capable of being chemically acted on by it in any way, the calorimeter was filled with oil of turpentine. The different substances enumerated in the table are arranged in groups according to their chemical composition.

Table of Specific Heats of Inorganic Compounds.

Name of Substance.	Formula.	Specific heat.	Molecular weight.	Product of sp. heat × mol. weight.
A.—DIATOMIC MOLECULES.				
1. *Oxides*	MO			
Protoxide of lead (fused)	PpbO	0·05089	223	11·35
Oxide of mercury	HhgO	·05179	216	11·19
Protoxide of manganese	MmnO	·15701	71	11·15
Oxide of copper	CcuO	·14201	79·5	11·19
Oxide of nickel (calcined)	NniO	·15885	74·7	11·87
Magnesia	MmgO	·24394	40	9·76
Oxide of zinc	ZznO	·12480	81	10·11
2. *Sulphides*	MS			
Protosulphide of iron	FfeS	·13570	88	11·94
Sulphide of nickel	NniS	·12813	90·7	11·62
„ cobalt	CcoS	·12512	90·7	11·36
„ zinc	ZznS	·12303	97	11·93
„ lead	PpbS	·05086	239	12·15
„ mercury	HhgS	·05117	232	11·87
Stannous sulphide	SnS	·08375	150	12·56
3. *Chlorides*	MCl			
Chloride of lithium	LiCl	·28213	42·5	11·99
„ sodium	NaCl	·21401	58·5	12·52
„ potassium	KCl	·17295	74·5	12·88
„ silver	AgCl	·09109	143·5	13·07
Mercurous chloride	HhgCl	·05205	235·5	12·26
Cuprous „	CcuCl	·13827	99·0	13·69
4. *Bromides*	MBr			
Bromide of potassium	KBr	·11322	119	13·47
„ silver	AgBr	·07391	188	13·90
„ sodium	NaBr	·13842	103	14·26
5. *Iodides*	MI			
Iodide of potassium	KI	·08191	166	13·60
Iodide of sodium	NaI	·08684	150	13·03
Mercurous iodide	HhgI	·03949	327	12·91
Iodide of silver	AgI	·06159	235	14·47
Cuprous iodide	CcuI	·06869	190·5	13·09
B.—TRIATOMIC MOLECULES.				
1. *Oxides*	MO^2			
Stannic oxide	SnO^2	·09326	150	13·99

Table of Specific Heats of Inorganic Compounds—continued.

Name of Substance.	Formula	Specific heat.	Molecular weight.	Product of sp. heat × mol. weight.
TRIATOMIC MOLECULES *continued*—				
Titanic anhydride (artificial)	$\mathrm{TiO^2}$	0·17164	82	14·07
" " (rutile)		·17032		13·97
Silicic anhydride	$\mathrm{SiO^2}$	·19132	60	11·48
Intermediate oxide of antimony	$\mathrm{SbO^2}$	·09535	154	14·70
2. *Sulphides*	$\mathrm{MS^2}$			
Iron pyrites	$\mathrm{FfeS^2}$	·13009	120	15·61
Stannic sulphide	$\mathrm{SnS^2}$	·11932	182	21·72
Disulphide of molybdenum	$\mathrm{MmoS^2}$	·12334	160	19·73
3. *Chlorides*				
Chloride of barium	$\mathrm{BbaCl^2}$	·08957	208	18·63
" strontium	$\mathrm{SsrCl^2}$	·11990	158·6	19·02
" calcium	$\mathrm{CcaCl^2}$	·16420	111	18·23
" magnesium	$\mathrm{MmgCl^2}$	·19460	95	18·49
" mercury	$\mathrm{HhgCl^2}$	·06889	271	18·67
" zinc	$\mathrm{ZznCl^2}$	·13618	136	18·52
" lead	$\mathrm{PpbCl^2}$	·06641	278	18·46
" manganese	MmnCl	·14255	126	17·96
Stannous chloride	$\mathrm{SnCl^2}$	·10161	189	19·20
4. *Iodides*	$\mathrm{MI^2}$			
Iodide of lead	$\mathrm{PpbI^2}$	·04267	461	19·65
" mercury	$\mathrm{HhgI^2}$	·04197	454	19·07
C.—TETRATOMIC MOLECULES.				
1. *Oxides*	$\mathrm{MO^3}$			
Tungstic anhydride	$\mathrm{WwoO^3}$	·07983	232	18·52
Molybdic anhydride	$\mathrm{MmoO^3}$	·13240	144	19·07
2. *Chlorides*	$\mathrm{MCl^3}$			
Chloride of arsenic	$\mathrm{AsCl^3}$	·17604	181·5	31·95
Trichloride of phosphorus	$\mathrm{PCl^3}$	·20922	137·5	28·77
D.—PENTATOMIC MOLECULES.				
1. *Simple oxides*	$\mathrm{M^2O^3}$			
Alumina corundum	$\mathrm{All^2O^3}$	·19762	103	20·35
Alumina sapphire		·21732		22·38
Specular iron	$\mathrm{Ffe^2O^3}$	·16695	160	26·71
Arsenious anhydride	$\mathrm{As^2O^3}$	·12786	198	23·01
Oxide of chromium	$\mathrm{Ccr^2O^3}$	·17960	153	27·47
" bismuth	$\mathrm{Bi^2O^3}$	·06053	468	28·33
" antimony	$\mathrm{Sb^2O^3}$	·09009	292	26·31
2. *Mixed oxides*	$\mathrm{MNO^3}$			
a. Nitrates.				
Nitrate of potassium	$\mathrm{NKO^3}$	·23875	101	24·11
" sodium	$\mathrm{NNaO^3}$	·27821	85	23·65
" silver	$\mathrm{NAgO^3}$	·14352	170	24·39
b. Carbonates.				
Carbonate of calcium Iceland spar	$\mathrm{CCcaO^3}$	·20858	100	20·86
Carbonate of calcium Arragonite		·20850		20·85
Carbonate of calcium saccharoïd marble		·21585		21·58
Carbonate of calcium " " grey		·20989		20·99
Carbonate of calcium white chalk		·21485		21·48
Carbonate of barium	$\mathrm{CBbaO^3}$	·11038	197	21·74
" strontium	$\mathrm{CSsrO^3}$	·14483	147·6	21·38
" iron	$\mathrm{CFfeO^3}$	·19345	116	22·44
3. *Sulphides*	$\mathrm{M^2S^3}$			
Sulphide of antimony	$\mathrm{Sb^2S^3}$	·08403	340	23·57
" bismuth	$\mathrm{Bi^2S^3}$	·06002	516	30·97
4. *Chlorides*	$\mathrm{MCl^4}$			
Stannic chloride	$\mathrm{SnCl^4}$	·14759	260	38·37
Chloride of titanium	$\mathrm{TiCl^4}$	·19145	192	36·76

Table of Specific Heats of Inorganic Compounds—continued.

Name of Substance.	Formula.	Specific heat.	Molecular weight.	Product of sp. heat × mol. weight.
E.—HEXATOMIC MOLECULES.				
1. *Sulphates*	SMO^4			
Sulphate of barium . . .	$SBbaO^4$	0·11285	238	26·28
„ strontium . .	$SSsrO^4$	·14279	183·6	26·36
„ calcium . . .	$SCcaO^4$	·19656	136	26·73
„ lead . . .	$SPpbO^4$	·08723	303	26·43
„ magnesium . .	$SMmgO^4$	·22159	120	26·59
2. *Carbonates*	CM^2O^3			
Carbonate of potassium . .	CK^2O^3	·21623	138	29·84
„ sodium . .	CNa^2O^3	·27275	106	28·91
F.—HEPTATOMIC MOLECULES.				
1. *Sulphates*	SM^2O^4			
Sulphate of potassium . .	SK^2O^4	·19010	174	33·08
„ sodium . . .	SNa^2O^4	·23115	142	32·82

For a numerous series of determinations of the specific heats of the isomorphous sulphates of the magnesian group, see Pape (Pogg. Ann. cxx. 337).

With regard to alloys of two or more metals, Regnault found that, at temperatures considerably removed from their melting points, their specific heats are the means of the specific heats of their components. In the following table, the values given in the column headed "Calculated Specific Heats" are obtained by multiplying the specific heat of each constituent into the percentage amount of it contained in the alloy, and dividing the sum of all these products for each alloy by 100; these values, therefore, would exactly represent the specific heats of the respective alloys if the above rule were rigorously true; the correspondence between them and the results of direct observation is sufficient to show that the rule is, at least, a close approximation to the truth.

Specific Heat of Alloys.

Composition of Alloy.	Observed specific heat.	Calculated specific heat.
1 at. lead + 1 at. tin	0·04073	0·04039
1 „ + 2 at. tin	·04506	·04461
1 „ + 1 at. antimony . . .	·03880	·03883
1 at. bismuth + 1 at. tin	·04000	·03987
1 „ + 2 at. tin	·04504	·04415
1 „ + 2 at. tin + 1 at. antimony.	·04621	·04564
1 „ + 2 at. tin + 1 at. antimony + 2 at. zinc . . .	·05657	·05479

In the case of alloys which, at the temperature of observation, were approaching their melting points, the observed specific heat was always considerably higher than that calculated as above.

The specific heats of a few liquids are included in the tables already given (pp. 30 and 32): we append here the results obtained by Person (Ann. Ch. Phys. [3] xxi. 333; xxiv. 136), H. Kopp (Pogg. Ann. lxxv. 98) and Favre and Silbermann (Comptes rend. xxiii. 524; also Ann. Ch. Phys. [3] xxxvii. 464–470), for some additional liquids, simple and compound. Favre and Silbermann's experiments were made by cooling the liquids in the mercurial calorimeter (p. 28), from their respective boiling points to temperatures nearly equal to that of the surrounding atmosphere.

Specific Heats of Liquids.

Liquids.	Temperature.	Specific heat.	Observers.
Lead	350° to 450°	0·0402	Person
Sulphur	120 „ 150	·234	„
Bismuth	280 „ 380	·0363	„
Tin	250 „ 350	·0637	„
Crystallised chloride of calcium	33 „ 80	·555	„
Nitrate of sodium . .	320 „ 430	·413	„
Nitrate of potassium . .	350 „ 435	·3319	„
Mercury	44 „ 24	·0332	Kopp
Iodine	. . . .	·10822	F. S.
Bromine	45 „ 11	·107	Andrews
Sulphuric acid . . .	46 „ 21	·343	Kopp
Wood-spirit . . .	43 „ 23	·645	„
		·6713	F. S.
Alcohol	43 „ 23	·615	Kopp
		·6438	F. S.
Fusel-oil	44 „ 26	·564	Kopp
		·5873	F. S.
Ethal	. . . .	·5059	„
Ether	. . . .	·50342	„
Formic acid	45 „ 24	·536	Kopp
Acetic acid	45 „ 24	·509	„
Butyric acid	45 „ 21	·503	„
Formate of ethyl . . .	39 „ 20	·513	„
Acetate of methyl . .	41 „ 21	·507	„
Acetate of ethyl . . .	45 „ 21	·496	„
		·48344	F. S.
Butyrate of methyl . .	45 „ 21	·487	Kopp
		·49176	F. S.
Valerate of methyl . .	45 „ 21	·491	Kopp
Acetone	41 „ 20	·530	„
Benzene	46 „ 19	·450	„
Oil of mustard . . .	48 „ 28	·432	„
Oil of turpentine . .	. . . .	·46727	F. S.

The specific heat of water at different temperatures has been determined by Regnault (Mém. Acad. Sciences, xxi. 729) from whose experiments it appears that the quantity of heat expressed in *heat-units* which one gramme of water loses in cooling down from t° to 0° C. is given by the formula,—

$$Q = t + 0{\cdot}00002\,t^2 + 0{\cdot}0000003\,t^3;$$

and the specific heat C at the temperature t°, that is to say, the quantity of heat required to raise one gramme of water from t° to $(t + 1)^\circ$, is:

$$C = 1 + 0{\cdot}00004\,t + 0{\cdot}0000009\,t^2.$$

From this formula, the following numbers are obtained:

Specific Heat of Water.

t.	Q.	C.	*t.*	Q.	C.
0°	0·000	1·0000	150°	151·462	1·0262
50	50·087	1·0042	200	203·200	1·0440
100	100·500	1·0130	230	234·708	1·0568

The specific heat of ice is considerably less than that of liquid water. According to Regnault's experiments, it is 0·474 between −78° and 0° C., and 0·504 between −20° and 0°, according to the experiments of Person and of Desains.

It results from Regnault's determinations of the specific heats of gases and vapours, made in the manner already mentioned (p. 29), that the specific heat of a given *weight* of a gas which obeys Boyle's law (Gases, ii. 820) does not alter with variations either of temperature or of pressure. This was found to be true of atmospheric air between the temperatures of $-20°$ and $+225°$, and at pressures varying from 1 to 12 atmospheres. Consequently the specific heat of a given *volume* of air, or other non-condensable gas, varies directly as its density. In gases which do not follow Boyle's law, this regularity does not exist: thus the specific heat of carbonic anhydride is found to increase perceptibly as its temperature rises, being 0·18427 between $-30°$ and 10°, and 0·20246 between 10° and 100°, and 0·21692 between 10° and 210°, as compared with that of an equal weight of water.

The following table gives the specific heats of the various gases and vapours examined by Regnault, compared, first, with an equal weight of water taken as unity, secondly, with that of an equal volume of air referred as before to its own weight of water as unity. The latter series of numbers is obtained by multiplying the numbers expressing the specific heats of equal weights of the various gases or vapours, by their respective densities referred to that of air as 1.

Table of Specific Heats of Gases and Vapours. (Regnault.)

Name.		Specific heats.	
		Equal weights.	Equal volumes.
Simple or mixed gases	Air	0·2374	0·2374
	Oxygen	·2175	·2405
	Nitrogen	·2438	·2370
	Hydrogen	3·4090	·2359
	Chlorine	·1210	·2962
	Bromine	·0555	·2991
Compound gases	Nitrous oxide	·2238	·3447
	Nitric oxide	·2315	·2406
	Carbonic oxide	·2450	·2370
	Carbonic anhydride	·2163	·3307
	Sulphurous anhydride	·1544	·3414
	Hydrochloric acid	·1845	·2333
	Sulphydric acid	·2431	·2857
	Ammonia	·5083	·2996
	Marsh-gas	·5929	·3277
	Olefiant gas	·4040	·4106
Vapours	Water	·4805	·2984
	Sulphide of carbon	·1570	·4140
	Alcohol	·4534	·7171
	Ether	·4810	1·2296
	Chloride of ethyl	·2737	·6096
	Bromide of ethyl	·1816	·6777
	Sulphide of ethyl	·4005	1·2568
	Cyanide of ethyl	·4261	·8105*
	Chloroform	·1566	·6565*
	Chloride of ethylene	·2293	·7911
	Acetate of ethyl	·4008	1·2184
	Acetone	·4125	·8341
	Benzene	·3754	1·0114
	Oil of turpentine	·5061	2·3776
	Trichloride of phosphorus	·1346	·6386
	Chloride of arsenic	·1122	·7013
	Chloride of silicon	·1329	·7788
	Stannic chloride	·0939	·8639
	Chloride of titanium	·1263	·8634

NOTE.—The numbers marked thus * in the last column are corrected for errors of calculation, pointed out by Clausius. (Ann. Ch. Pharm. cxviii. pp. 114, 115, and 118, 119, foot-notes.)

Comparing these values with those given for some of the same substances in previous tables, it appears that the specific heat of the same body is commonly greater in the liquid than in the solid state, and always less in the gaseous, than in the liquid state.

On examining the numbers above given for the specific heats of different bodies, it will be seen that the specific heat of a substance is not altogether an absolute and unchangeable property: on the contrary, it will be evident that this property, in one and the same substance, is capable of considerable variation, depending (*a*) on the physical structure of the substance, (*b*) on its temperature, (*c*) on its state of aggregation. In illustration of this remark, it will be sufficient to refer to the specific heats of carbon, silicon, selenium, sulphur, phosphorus, alumina, and carbonate of calcium, as given in the foregoing tables, in evidence of the influence of differences of physical condition; to the specific heats of lead, phosphorus, water, and ice, in evidence of the effect of differences of temperature; and to those of bromine, mercury, tin, lead, bismuth, water, &c., in the solid and liquid states, in evidence of the effect of the state of aggregation.

In reference to the connection between specific heat and temperature, it may be remarked that this property varies to a greater extent, for a given interval of temperature, near the temperatures at which changes in the state of aggregation occur, than at a distance from those temperatures. Thus, the specific heat of lead, an easily fusible metal, is considerably greater between 10° and 100° C. (=0·0314) than it is between 10° and −78° C. (=0·0306); and that of phosphorus, a still more fusible substance, shows even a greater difference when compared between 10° and 30° (specific heat = 0·1887) and between −71° and 10° C. (specific heat = 0·1740); while the specific heat of platinum, one of the most infusible of all the metals, varies to a scarcely perceptible extent at temperatures below 100° C., and only slowly at temperatures considerably higher. The mean specific heat of this metal between 0° C. and the temperatures enumerated below, was in fact found by Pouillet to be represented by the numbers contained in the second line of the following table.

Specific Heat of Platinum.

Interval of temperature	0° and 100°	0° and 300°	0° and 500°	0° and 700°	0° and 1000°	0° and 1200°
Mean specific heat .	0·0335	0·03434	0·03518	0·03602	0·03728	0·03·08

The specific heat of solid bodies therefore increases with rise of temperature, up to their melting points, and at this temperature there is generally a further sudden increase of specific heat of a considerable amount.

It may be further noticed that in the table of the specific heats of the elements (p. 30), the elements are arranged nearly in the order of their specific heats, beginning with lithium (specific heat = 0·941) and ending (if we disregard for the present the three elements carbon, boron, and silicon, which are placed together after the rest) with bismuth (specific heat 0·031); and that this order is also exactly the inverse order of their atomic weights, as given in the fourth column, the atomic weight of lithium (=7) being less than that of any other element included in the table, and that of bismuth (= 210) being greater than that of any other element. In fact, not only do those elements whose atomic weight is lowest possess, as a rule, the greatest specific heat, and *vice versâ*, but the specific heats of the elements (in the solid state) are, within comparatively narrow limits, inversely proportional to their atomic weights, when these are taken as having the values given in the fourth column of the table; so that the product of the specific heats of the elements into their atomic weights is nearly a constant quantity; as shown by the numbers in the fifth column of the table. These numbers may be taken to represent the *atomic heats* of the elements, or the relative quantities of heat which must be imparted to, or removed from, atomic proportions of the several elements, in order to cause in them equal alterations of temperature. The table shows that the atomic heats of the elements are not represented by an absolutely constant quantity; but when it is considered that the two factors (atomic weight and specific heat) of which they are made up, vary in the proportion of 1 : 30, it cannot be denied that they are comprised between comparatively very narrow limits: for (taking those determinations only which refer to comparable conditions of the several elements, and which there is reason to believe were made upon nearly pure substances) we find that they are nearly all included between 5·9 (aluminium, rhodium) and 6·9 (iodine), the greater number not differing much from 6·5. (The high atomic heat of uranium, 7·4, is doubtless to be explained by the impurity of the metal operated upon.) The general accordance is amply sufficient to indicate the existence of a general law, although the individual results show the effect of some one or more disturbing causes. And even if it be admitted that the true atomic heats of the elements under consideration are really identical, under comparable circumstances, there are several reasons why the experimental atomic heats, deduced like those in the foregoing table, cannot be expected to exhibit the same identity. The most important of these reasons are: the unavoidable experimental errors attaching to the determination of the specific heats; the imperfect purity of some of the elements examined; the circumstance that, although most of the determinations were made at nearly the same absolute temperatures—namely, between a temperature near 100° and that of the atmosphere—the different elements are not, in regard to their specific heats, under comparable circumstances at these temperatures, some being much nearer to their melting point than others, and therefore having in general relatively higher specific heats (see p. 36); lastly, in a few cases, the uncertainty of the experimental data used in fixing the atomic weights.

The relation of approximate equality among the atomic heats of the elements exists, however, only when their atomic weights are allowed to have the values given in the table: these values are in very many cases the double of those which are given in the table of atomic weights, vol. i. pp. 464, 465, and are employed throughout this work. If the latter scale of atomic weights be adopted, the elements would have to be divided into two classes: those whose atomic heat is approximately 6·5, and those whose atomic heat is approximately 3·2. The fact that, by doubling the atomic weights of the latter class of elements, their atomic heats would be brought into harmony with those of the former class, is in itself a strong argument in favour of such a change; and by reference to the articles ATOMIC WEIGHTS (i. 468—473) and CLASSIFICATION (i. 1008, 1009, foot-note) it will be seen that it is supported by many other considerations, both chemical and physical. In any case it is certain that the numbers in the column headed "Atomic Weights," in the table on p. 30, represent quantities of the various elements which are calorimetrically comparable; and it is therefore convenient, while considering the present subject, to assume these numbers as really representing those weights of the elements which, in relation to the phenomena of heat, possess the properties of atoms. Whether the chemical atoms of the elements are always identical with the calorimetric atoms, is a question that is perhaps still open to discussion.

It is very important, however, not to overlook the fact that the atomic heats of boron, carbon, and silicon form unquestionable exceptions to the general rule, and cannot be brought into harmony with it, by the adoption of any atomic weights to which the present state of chemical knowledge lends any serious support.

The examples which have been given (pp. 31–33) of the specific heats of compound bodies, show that, within certain classes of allied compounds, the same kind of relation subsists between their specific heats and molecular weights, as has been pointed out between the specific heats and atomic weights of the elements. Consequently, the molecular heats of the substances comprised in each such class, or the products of their specific heats into their molecular weights (see the last column of the table), are approximately equal. In calculating these molecular heats, the atomic weights of the elements are taken as having the values which may be deduced from their specific heats; those values, namely, which are given in the previous table. When these atomic weights are twice as great as those commonly adopted, they are denoted by the reduplication of the first consonant of the ordinary symbol: thus, All = Al^2, Ffe = Fe^2, Ppb = Pb^2, &c. Adopting these atomic weights, it will be seen that, as a rule, the molecular heat of solid compound bodies increases with the number of atoms contained in their molecule. For instance, the molecular heat of the oxides MO enumerated in the table averages about 11; that of the oxides MO^2, about 14; that of the oxides MO^3, about 19; that of the oxides M^2O^3, about 25·5.

An extensive series of determinations of the specific heats of solid bodies has been made by H. Kopp, but the individual results have not yet been published; we shall, therefore, instead of discussing any further the relations between specific heat and chemical composition which might be deduced from Regnault's experiments already given, reproduce here the substance of the remarks which Kopp (Ann. Ch. Pharm. cxxvi. 362), with his own results before him, makes upon this subject.

This new investigation has brought to light a considerable number of additional examples of solid compounds which, having an analogous atomic constitution, possess also approximatively the same molecular heat. Among these, particular interest attaches to the case in which an analogy of constitution is apparent only when the atomic weights of the elements are admitted to have the values assigned to them in the foregoing tables, and where the formulæ previously adopted and the old atomic weights of the elements would never have caused any such relations between specific heat and molecular weight to be suspected. Just as the molecular heats of carbonates and silicates, $M''CO^3$ and $M''SiO^3$, and of nitrates and chlorates, MNO^3 and $MClO^3$, are approximately equal, so also are the molecular heats of the permanganates and perchlorates, $MMmnO^4$ and $MClO^4$, and of the sulphates and chromates, $M''SO^4$ and $M''CcrO^4$. The new investigation, however, also furnishes some additional examples to the previously known exceptions to the general rule, and thus supplies further evidence of the fact that it is possible for bodies of analogous constitution to differ considerably in their molecular heats.

The molecular heat of a compound appears to be governed only by its empirical, and not by its rational constitution. Analogous compounds, in one of which a complex group occupies the place of an elementary atom, were found, even when isomorphous, to have unequal molecular heats; thus the molecular heats of the ammonium-compounds are considerably greater than those of the corresponding potassium-compounds, and those of the cyanogen-compounds exceed those of the chlorine-compounds.

The atomic (or molecular) heat of any body which is contained in a compound, or may be assumed as one of its constituents, may accordingly be ascertained indirectly, by deducting from the molecular heat of the compound that of whatever other constituents it contains in addition to the body in question. For instance, if we deduct from the molecular heat of a compound of the form $M''M''O^4$ (chromate of lead, tungstate of calcium, &c.)—which, it may be remarked, is twice as great as that of compounds of the form $M''O^2$ (stannic oxide, titanic anhydride, &c.)—the molecular heat of the base $M''O$, we get as remainder the molecular heat of the anhydrous acid $M''O^3$; and the same remainder is obtained by deducting, from the molecular heat of acid chromate of potassium, $K^2Ccr^2O^7$, that of the neutral chromate, K^2CcrO^4. Again: the molecular heats of hydrated compounds admit of being regarded as made up of the molecular heat of the respective anhydrous substances, together with that of the water contained in them in the solid form.

Such indirect determinations of the atomic heat of a substance are nevertheless somewhat uncertain: not only because it occasionally happens that analogous compounds, which there is every reason to expect would possess equal molecular heats, do nevertheless, according to the experimental determinations of their specific heats, show important differences in their molecular heats; but also, and more particularly, because the total uncertainty attaching to the determination of the molecular heat, both of the original compound and of the element or group which has to be deducted from it, is accumulated upon the relatively small remainder. But when such inferential determinations are made for whole series of corresponding bodies, and not merely for individual cases, the results may be regarded as sufficiently trustworthy to render such considerations as arise from them worthy of notice.

This is especially the case with regard to the inferred specific and atomic heats of certain elements. As already pointed out, nearly all the elements, when examined in the solid state, are found to have approximately the same atomic heat—on the average, about 6·4. It is now very generally admitted that this—the so-called law of Dulong and Petit—holds good for *all* the elements, and a scale of atomic weights of the elements is considered as satisfactorily established if the products of these atomic weights into the specific heats are nearly equal. In the case of some elements, however, it results, both from the older determinations of their specific heats and from Kopp's newer determinations, that this rule is inapplicable; for example, the specific heats of carbon, boron, and silicon, are such, that the products, obtained by multiplying them into the respective atomic weights—when any values are adopted for these which can possibly be deduced from chemical considerations—are always decidedly smaller than the corresponding products in the case of other elements whose specific heats in the solid state can be investigated.

But these exceptional or accidental results acquire additional interest when taken in connection with the conclusions which may be drawn from the molecular heats of compounds. Compounds of those elements which obey Dulong and Petit's law exhibit a regularity in their molecular heats (*A. H.*): such, namely, that these are as many times greater than that of an element, as there are elementary atoms contained in the respective compounds (that is to say, $\frac{A.H.}{n} = 6\cdot4$ nearly, if n denotes the number of elementary atoms in one molecule of each compound). This regularity appears, not only in alloys containing atomic proportions of different metals, but also in the metallic chlorides, bromides, and iodides (see table, pp. 31, 32), and has been found by Kopp to extend likewise to compounds of which one molecule contains as many as seven, or even nine, elementary atoms (such as $ZznK^2Cl^4$ and $PptK^2Cl^6$). It is less distinctly recognisable in the case of the compounds of the metals with sulphur ($\frac{A.H.}{n}$ is here usually less than 6), and no longer exists for the metallic oxides, which, almost without exception, give for the quotient $\frac{A.H.}{n}$ a number decidedly less than 6, and smaller in proportion as the number of oxygen-atoms exceeds that of the atoms of metal. For water, considered of course in the solid state, this quotient is only about 3, and for the few organic compounds which Kopp has examined (such as tartaric acid and cane-sugar) it is still less.

The fact that this regularity is absent in so many compounds admits of only one explanation—namely, that they contain elements which, at least in these combinations, possess a different atomic heat from that which corresponds to Dulong and Petit's law.

It has often been assumed that the specific, and therefore the atomic, heat of an element may be different in certain compounds from what it is in the free state, and that it may be different in one compound from what it is in another. But, according to Kopp, the only ground for such an assumption is that by means of it the calculated molecular heats of compound bodies can be brought into closer agreement with the results of experiment; for, as he remarks, the variations which the specific heat of an element must be supposed capable of undergoing when it enters into combination (if Dulong and Petit's law be taken as applicable to all elements in the free state) are much greater than the variations, dependent on differences of physical condition, which have ever been actually observed in the case of an accurately investigated element. On the contrary, it appears that, in many compounds, the elementary atoms of which they are composed retain the atomic heats which belong to them in the free state; and that, moreover, the atomic heats which can be indirectly calculated for certain elements, notwithstanding their disagreement with Dulong and Petit's law, accord very closely with the atomic heats which result from the direct investigation of the same elements in the free state. Kopp accordingly maintains that—although these last-mentioned facts render the calculation of the molecular heat, and thence of the specific heat, of compound bodies from the atomic heats of the elements much more difficult, and although they make the agreement between the results of calculation and those of direct observation much less complete—every element, when considered in the solid state, and at a temperature sufficiently removed from its melting point, possesses one essentially invariable specific heat, which it is true may vary somewhat with differences of physical condition—such as greater or less density, amorphous or crystalline structure, &c.—but not to such an extent as some of his determinations of specific heat would require, if Dulong and Petit's law were really applicable to all the elements; and further, that the specific heat of each element in the free state is essentially the same as that which it possesses in its compounds.

By deducting from the molecular heats of the various oxides the atomic heats of the metals contained in them, or by deducting from the molecular heats of the oxygen-salts those of the groups which are therein united with oxygen (taking away from the molecular heat of $KClO^3$, for example, that of KCl, or from that of $PpbSO^4$ the molecular heat of PpbS), a remainder is obtained in every case which gives for the atomic heat of oxygen a number less than 6. For the reasons already stated (p. 38), the results thus arrived at do not agree so well as might be wished; nevertheless, Kopp gives it as his opinion that the atomic heat of oxygen cannot differ greatly from 4.

When the molecular heats of the carbonates M^2CO^3 and $M''CO^3$ are compared with the molecular heats of the oxides $(M'')^3O^3$ (= $3M''O$) and $(M'')^2O^2$, the molecular heats of the carbonates are found to be decidedly smaller (according to Regnault's experiments, as given in the table, pp. 31–33, the molecular heats of the carbonates $M{\cdot}CO^3$ and oxides $3M''O$ are, on the average, about 29·4 and 32·85 respectively; those of the carbonates $M''CO^3$ and oxides $(M'')^2O^2$, about 21·7 and 25·5 respectively). Such comparisons show that the atomic heat of carbon in these combinations must be assumed to be about the same as that which has been directly found for free carbon in the form of diamond; namely, 1·8. Similar comparisons applied to other elements lead likewise to the adoption of atomic heats which are much smaller than what would correspond to the law of Dulong and Petit: for instance, to the atomic heat 2·3 (nearly) for hydrogen; for boron, to a number lying between 2 and 3; for silicon, to 4 (nearly); and for fluorine, also to a number which appears to be distinctly less than 6·4.

The specific and molecular heats of compound bodies calculated with the atomic heats thus arrived at for the elements, show, in very many cases, a very satisfactory degree of agreement with those deduced from direct experiment; in many other cases, however, they show important discrepancies. But equal discrepancies may likewise be observed among the molecular heats of analogous compounds, such even as contain elements as corresponding constituents which, when examined in the free state, gave nearly equal atomic heats. Regnault not unfrequently found this difference amount to one-tenth of the molecular heats in question; occasionally it was still greater.

Kopp considers that the results of his investigation confirm and widen the conclusion, already adopted by some philosophers, that Dulong and Petit's law does not hold good for all the so-called elements in the solid state. For a particular group of elements it is undoubtedly true; but if it is not a universal law, and if there are some elements to which it certainly does not apply, it may be considered doubtful with regard to individual elements, whether they ought to be looked upon as agreeing with or as departing from it. This may be said to be the case with sulphur, for which Kopp's determinations, made between 47° and the temperature of the atmosphere, give the atomic heat 5·2, nearly, which likewise agrees with the atomic heat of sulphur as indirectly deduced from the molecular heats of the metallic sulphides.

In general, the molecular heat of a compound increases with its degree of complexity, or with the number of elementary atoms contained in one molecule, and this more especially in the case of such as contain only elements which follow Dulong and Petit's law. Kopp points out that if the application of this rule be extended to the elements themselves, the fact that a large proportion of them have nearly the same atomic heat may be taken as an indication that, whether they be absolutely simple substances or no, they are at least bodies of a comparable degree of complexity; while, on the other hand, the smaller atomic heats of some elements would seem to show that they are of a lower degree of complexity, or approach more nearly to truly simple bodies, than the rest. It would thus appear to be possible for a substance which can be proved to be compound, to have the same atomic heat as a so-called element: for instance, a peroxide, XO, containing an element whose atomic heat was equal to that of hydrogen, namely, about 2·3, would have a molecular heat of about $2·3 + 4 = 6·3$, that is to say, the same as that of chlorine, iodine, or the metals.

With regard to the apparent improbability of two so-called elements, which are capable of mutually replacing each other in compounds, like hydrogen and the metals—or which even appear as corresponding constituents of isomorphous substances, like silicon and tin—having unequal atomic heats, it must be borne in mind that this is not in reality any more surprising or improbable than that an undecomposible substance and one known to be compound, such, for example, as hydrogen and peroxide of nitrogen, or potassium and ammonium, should replace each other in compound bodies without causing any alteration in their chemical characters, or should even be capable of appearing as corresponding constituents of isomorphous substances.

It still remains to consider, rather more particularly than has been done thus far, what it is that is measured under the name of the specific heat of solid, liquid, or gaseous substances, by the methods above described.

In all these methods of measurement, the heat imparted to the various bodies does something more than merely raise their temperature: it causes at the same time, as will be seen by what follows, an expansion or increase of their bulk; and when the bodies are again cooled, they contract, or diminish in bulk, to an equal amount. Hence the specific heats, measured as above, are not, strictly speaking, the relative quantities of heat required to raise the temperature of the various substances to the same extent, but the quantities required to do this, *and* at the same time to cause a greater or less increase of bulk. It is therefore a question for further investigation, what proportion of the total specific heat of a substance goes to raise its temperature, and what proportion to cause it to expand, or possibly to modify it in other ways.

The expansion which accompanies a given rise of temperature is inconsiderable in the case of solids and liquids, compared with that which takes place in gases; but it would be incorrect to conclude that the proportion of the total specific heat of solid, liquid and gaseous substances respectively, which is expended in causing expansion, is in proportion to the amount of expansion actually produced in each case. On the other hand, although no data exist which make it possible to form a very definite estimate of the ratio of the *real* specific heat to the *total apparent* specific heat of solids or liquids (see, however, p. 44), it is certain that they oppose a much greater resistance to any force tending to alter their bulk than gases do, and hence the comparatively small amount of expansion which they undergo may require the expenditure of as much or more heat than the relatively great expansion which takes place in gases: there is, therefore, no reason to believe that the ratio of the two specific heats, in the case of solid and liquid substances, is a magnitude of a different order from what it is in the case of gases.

The ratio of the apparent to the real specific heat of a gas, is the ratio of its specific heat under constant pressure (when, therefore, it expands as the temperature rises) to its specific heat when kept at a constant volume. It is, of course, the specific heat under constant pressure which is determined by the method already described (p. 29), and which is given for several gases in one of the preceding tables (p. 35). That the specific heat of a gas kept at a constant volume is less than its specific heat under a constant pressure, is obvious from the following considerations. Suppose a quantity of gas to have had its temperature raised t°, while the pressure to which it was exposed remained constant: the increase of temperature will have been accompanied by a corresponding increase of volume. Now, suppose the gas to be compressed, so as to restore it to its original bulk: the result of this compression will be to raise its temperature t'° more. The gas will now be in the same condition as it would have been if the same quantity of heat had been imparted to it without its being allowed to expand: hence it is evident that the same quantity of heat that is required to raise the temperature of a given weight of gas t°, while the pressure remains constant, will suffice to raise the temperature of the gas $t + t'$ degrees if it is kept at a constant volume. The specific heat, c', corresponding to a constant pressure, is therefore to the specific heat, c, corresponding to a constant volume, as $t + t'$ to t. One gramme of air has its temperature raised 1° C. when there is imparted to it 0·2374 of a unit (gramme-degree) of heat, and it expands at the same time, if the pressure remains unaltered, by $\frac{1}{273}$ of its bulk at 0° C. Accordingly, if the elevation of temperature consequent on compressing a gas by $\frac{1}{273}$ of its bulk at 0° be $\alpha°$, it is evident that the ratio

$$\frac{1 + \alpha}{1} = \frac{c'}{c} = k$$

is the ratio of the specific heat under constant pressure to that at constant volume. Clement and Desormes found by direct experiments upon air the value 0·34° for α, but it is plain that the unavoidable loss of heat attending such experiments must cause the result to be too low.

A less direct, but far more accurate means of determining the ratio $k = \frac{c'}{c}$, not only for air but for several other gases also, is afforded by the theory of the propagation of sound. The velocity with which a wave-motion, such as that which constitutes sound, is propagated through a homogeneous medium whose elasticity is the same in all directions, depends only upon the elasticity, e (see ii. 370), and the density, d, of the medium, according to the equation

$$v = \sqrt{\frac{e}{d}}.$$

This expression, applied to the movement of a sound-wave through the air, becomes

$$v = \sqrt{\frac{e}{d}} = \sqrt{\frac{gH\sigma}{s}.\,k\,(1 + \alpha\, t)};$$

where g denotes the accelerating force of gravity (= 9·808 metres = 32·18 feet); H = 760 mm. = 29·92 inches; σ the weight of 1 cub. cent. of mercury at 0° = 13·596 grm.; s the weight of 1 cub. cent. of air at 0° and under a pressure of 760 mm. mercury = 0·001293 grm.; t the temperature of the air, α its coefficient of expansion under constant pressure (= 0·00367), and k the required ratio $\frac{c'}{c}$. Now the velocity of sound in air at 0° has been experimentally found to be = 333 metres, or 1092·6 feet per second; hence the above equation gives

$$333 = \sqrt{\frac{9{\cdot}808 \times 0{\cdot}76 \times 13{\cdot}596}{0{\cdot}001293}.\,k}$$

or $k = 1{\cdot}414$.

The physical reason for the presence of the magnitude k in the formula for the velocity of sound, is that that velocity, being dependent upon the elasticity of the air, varies with every variation of the elasticity, and that the alternate heatings and coolings, caused respectively by the alternate condensations and rarefactions which constitute the waves of sound, are equivalent, in their effect upon the velocity of transmission of the waves, to an increase in the elasticity of the air in the proportion of $1 : k = 1 : 1{\cdot}413$.

In the above formula the magnitudes g, H, σ t, and α are all independent of the particular nature of the gas (at least in the case of perfect gases; for imperfect gases the value of α varies slightly), hence if v and v' represent the velocities with which sound traverses two different gases, s and s' their densities, and k and k' the ratios of the two specific heats of each, we have

$$v : v' = \sqrt{\frac{k}{s}} : \sqrt{\frac{k'}{s'}},$$

$$\text{or} \sqrt{k'} = \frac{v'}{v} \sqrt{\frac{s'}{s}.\,k};$$

so that the ratio k' for any gas may be deduced from that of air, provided the density of the gas and the velocity with which it is traversed by sound are known.

Hence the investigation of this ratio is reduced to that of the real velocities of sound in different elastic fluids. For any other gas than atmospheric air, it is useless to think of measuring directly the velocity of propagation of a sonorous wave; recourse must obviously be had to indirect means. The theory of wind instruments suggested a mode, which was first indicated and put in practice by Chladni and Jacquin. This method consists in making the same pipe, with a flute *embouchure*, sound successively with all the elastic fluids, supposed at the same temperature, and in determining the pitch of tone given by each gas. Admitting that the fluid column contained in the instrument experiences the same mode of subdivision in every case—that it corresponds, for example, to what is called the fundamental sound, or the gravest of all those which the theory of Bernouilli indicates for the same pipe, we easily come to know the length of a wave, and its duration in each elastic fluid; and consequently the velocity with which a vibration would be propagated in each of them.

The following table exhibits the results of Dulong's researches on this subject. (Ann. Ch. Phys. xli. 113):

Names of the elastic fluids.	Tones given by the same pipe 60 centim. long.	Number of vibrations in a sexagesimal second.	Temperature by the centigrade therm.	Numbers adopted in the calculation for the density of the fluid.	Velocity of the propagation of sound at 0°, deduced from the tone given by each fluid.	Ratio of the specific heats at a constant pressure, to the specific heat at a constant volume, = *k*.
Air . . .	ut_1 med.	500·4	22°	1	333$^{\mathrm{m}}$	1·421
Oxygen . .	$+si_{-1}$	474·9 475·2 474·5	21	1·1026	317·17	1·415 1·417 1·413
Hydrogen .	$-si_3$	1883·6 1881·	17	0·0688	1269·5	1·409 1·405
Carbonic anhydride	sol_{-1}	393·18 392·68	22 20·5	1·524	261·6	1·357 1·340
Carbonic oxide	ut_1	501·3 503·07	15	0·974	337·4	1·423 1·433
Nitric oxide .	sol_{-1}	392·7	20·5	1·527	261·9	1·343
Olefiant gas .	$-si_{-1}$	466·9	16	0·981	314	1·240

The slight difference between the value 1·421, obtained by Dulong for the ratio of the two specific heats of air, and the number 1·414 already given is, in part, due to the changes which have taken place, since the date of his experiments, in the adopted value of the constants which enter into the calculation.

Theoretical views of the nature of heat and the constitution of gaseous bodies, which will have to be further considered in a subsequent part of this article, lead to the conclusion that, for all perfect gases, the difference between the two specific heats of a unit of volume is expressed by the equation

$$\gamma' - \gamma = A \frac{p}{a + t} \quad . \; . \; . \; . \; . \quad (a)$$

where A is a constant (the thermal equivalent of the unit of work), p and t the pressure and temperature of the gas, and $\frac{1}{a}$ the coefficient of expansion, and therefore $a = 273$ nearly. The right hand member of this equation contains nothing which depends on the particular nature of the gas to which it is applied; and hence, if the temperature and pressure are taken the same for all gases, the difference $\gamma' - \gamma$ will be the same for all. If the values of γ' and γ applicable to atmospheric air be distinguished as $\gamma'_{,}$ and $\gamma_{,}$, we have

$$\gamma' - \gamma = \gamma'_{,} - \gamma_{,}$$

an equation which remains true whatever unit of volume is adopted, and therefore also, if with Regnault, we take this unit to be the volume occupied by a unit of weight of air at the same temperature and pressure as the gas under consideration. Therefore

$$\gamma' - \gamma = \gamma'_{,} - \gamma_{,} = 0{\cdot}2374 - 0{\cdot}1680 = 0{\cdot}0694 \text{ and } \gamma = \gamma' - 0{\cdot}0694.$$

By means of this equation, the specific heats of the various gases under constant volume may be calculated from their specific heats under constant pressure as given in the table on p. 35. The numbers so obtained will refer to the unit of volume adopted by Regnault; to deduce therefrom the specific heats which correspond to a *unit of weight*, these numbers require merely to be divided by the densities of the respective gases; and to obtain the specific heats *compared with that of an equal volume of air*, they must be divided by 0·1680.

According to equation (*a*) the quotient $\frac{\gamma'}{\gamma} = k$ becomes

$$k = 1 + \frac{A}{\gamma} \cdot \frac{p}{a + t}$$

and it therefore exceeds unity by a quantity which is inversely proportional to γ.

Further, the general considerations above referred to make it probable that the true specific heat of equal volumes of all simple gases is the same, and that the specific heat of compound gases is equal to that of the simple gases multiplied by the fraction which represents their molecular condensation (*e.g.* for hydrochloric acid the multiplier would be $\frac{1 + 1}{2} = 1$, for water $\frac{2 + 1}{2} = 1·5$, for ammonia $\frac{3 + 1}{2} = 2$, &c.).

The following table, which is copied with very slight modifications from tables given by Clausius (Ann. Ch. Pharm. cxviii. 118) and Buff (*ibid.* cxv. 312; see also pp. 306, 307), and may be considered supplementary to the table on p. 35, gives the results of the application of these formulæ to the gases and vapours which were the

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
			Sp. heat of equal volumes under constant pressure Air=1.	Specific heat at constant volume.			True sp. heat compared with that of the elementary gases.
Name of gas.	Formula.	Density.		Equal weights. Water = 1.	Equal volumes. Air=1.	Value of $\frac{c'}{c} = k$.	
Air		1·0000	1·00	0·168	1·00	1·413	1·0
Oxygen	O^2	1·1056	1·01	·155	1·02	1·403	1·0
Nitrogen	N^2	·9713	1·00	·173	1·00	1·409	1·0
Hydrogen	H^2	·0692	·99	2·406	·99	1·417	1·0
Chlorine	Cl^2	2·4400	1·25	·093	1·35	. .	1·0
Bromine	Br^2	5·3900	1·26	·042	1·37	. .	1·0
Nitric oxide . . .	NO	1·0390	1·01	·165	1·02	1·403	1·0
Carbonic oxide . . .	CO	·9674	1·00	·173	1·00	1·416	1·0
Hydrochloric acid . .	HCl	1·2474	·98	·131	·98	. .	1·0
Nitrous oxide . . .	N^2O	1·5250	1·45	·180	1·64	1·243	1·5
Water	H^2O	·6210	1·26	·369	1·36	1·302	1·5
Sulphydric acid . . .	H^2S	1·1912	1·20	·182	1·29	. .	1·5
Carbonic anhydride . .	CO^2	1·5290	1·39	·171	1·55	1·265	1.5
Sulphurous anhydride .	SO^2	2·2470	1·44	·121	1·62	. .	1·5
Sulphide of carbon . .	CS^2	2·6325	1·74	·131	2·05	. .	1·5
Ammonia	NH^3	·5894	1·26	·391	1·37	. .	2·0
Marsh-gas	CH^4	·5527	1·38	·467	1·54	. .	2·5
Olefiant gas . . .	C^2H^4	·9672	1·73	·353	2·08	1·144	3·0
Alcohol	C^2H^6O	1·5890	3·02	·408	3·86	. .	4·5
Ether	$C^4H^{10}O$	2·5563	5·18	·454	6·91	1·059	7·5
Sulphide of ethyl . .	$C^4H^{10}S$	3·1380	5·29	·378	7·07	. .	7·5
Chloride of ethyl . .	C^2H^5Cl	2·2350	2·57	·242	3·22	. .	4·0
Bromide of ethyl . .	C^2H^5Br	3·7316	2·85	·163	3·62	. .	4·0
Cyanide of ethyl . .	C^3H^5N	1·9021	3·41	·332	4·41	. .	4·5
Chloroform . . .	$CHCl^3$	4·1920	2·76	·140	3·49	. .	2·5
Chloride of ethylene . .	$C^2H^4Cl^2$	3·4500	3·33	·209	4·30	. .	4·0
Acetate of ethyl . . .	$C^4H^8O^2$	3·0400	5·13	·378	6·84	. .	7·0
Acetone	C^3H^6O	2·0220	3·60	·378	4·55	. .	5·0
Benzene	C^6H^6	2·6943	4·26	·350	5·61	. .	6·0
Oil of turpentine . .	$C^{10}H^{16}$	4·6978	10·01	·491	13·74	. .	13·0
Trichloride of phosphorus .	PCl^3	4·7445	2·69	·120	3·39		
Chloride of arsenic . .	$AsCl^3$	6·2510	2·95	·101	3·76		
Chloride of silicon . .	$SiCl^4$	5·8600	3·28	·121	4·22		
Stannic chloride . .	$SnCl^4$	9·2000	3·64	·086	4·73		
Chloride of titanium . .	$TiCl^4$	6·8360	3·64	·116	4·73		

subject of Regnault's experiments. Column I. gives the *names* of the gases; column II. their *chemical composition:* the formulæ in this column represent *two* volumes of the several gases: hence the molecular condensation of each gas is obtained by dividing the number of atoms in its formula by 2. Column III. gives the *densities* adopted by Regnault in his calculations. Column IV. gives the specific heats under *constant pressure* compared with that of an equal volume of air taken as unity. The numbers in this column are obtained from those in the last column of the table on p. 35 by dividing each by 0·2374 = specific heat of air under constant pressure. Columns V. and VI. contain the specific heats corresponding to a *constant volume* compared (V.) with that of an equal weight of water, and (VI.) with that of an equal volume of air. Column VII. gives the *ratio of the two specific heats* for some of the most important gases, obtained by dividing the specific heats of equal weights under constant pressure, as given in the previous table (p. 35), by the corresponding values in column V. of this table. Column VIII. contains the theoretical *true specific heats*, compared with the true specific heat of an equal volume of air or any simple gas. These numbers are calculated upon the supposition that the true specific heats of the elementary gases are the same in the combined as in the uncombined state.

On comparing the numbers in columns VI. and VIII. it will be seen that there is, on the whole, an unmistakable correspondence between them, but that they exhibit also in many cases decided discrepancies. These are probably due, in part to errors of experiment, and in part to the fact that the method, by which the numbers representing the specific heats at constant volume are calculated from those representing the specific heats at constant pressure, is quite accurate only in the case of perfect gases; and further that, even if the numbers in column VI. represented the specific heats for constant volume with perfect accuracy, these numbers would not necessarily agree with those in column VIII., except for perfect gases.

The true specific heat of a gas, that is, its specific heat under a constant volume, is regarded by Clausius (Phil. Mag. [4] xxiv. 204, 205) as the true specific heat of the substance in all states of aggregation, and in the combined as well as the free state. Rankine, on the other hand (*A Manual of the Steam Engine*, &c., p. 307), while admitting that the true specific heat of each substance remains constant at all densities, so long as the substance retains the same condition, solid, liquid, or gaseous, supposes that a change of real specific heat, sometimes considerable, often accompanies the change between any two of these conditions. But, as Clausius has pointed out (*loc. cit.*; also Pogg. Ann. cxx. 438), there is no obvious reason why the real specific heat of a body should be supposed to undergo alteration on the passage from one state of aggregation to another, if it remains constant within the same state of aggregation; for the changes of density and elasticity, which accompany changes of temperature within one and the same state, do not differ in kind, but only in degree, from those which constitute the passage from one state to another. Assuming, therefore, that the specific heat under constant volume of a substance in the gaseous state is its real specific heat under all conditions, we have, for water, for instance,

Ratio of apparent to real specific heat in the *solid state* (between −20° and 0°) . . . . $= \frac{\cdot 504}{\cdot 369} = 1\cdot 367$

Ratio of apparent to real specific heat in the liquid state (between 0° and 100°) . . . . $= \frac{1\cdot 008}{\cdot 369} = 2\cdot 732$

Ratio of apparent to real specific heat in the gaseous state . $= \frac{\cdot 4805}{\cdot 369} = 1\cdot 302$

2. *Changes of Volume produced by Heat.*

It is an almost universal law that, when heat is imparted to any body, the body expands or augments in bulk, unless prevented from doing so by a corresponding increase of external pressure, and that any body from which heat is withdrawn contracts or diminishes in bulk. The exceptions to this law are extremely few, and occur only within particular limits of temperature: the most important will be specially pointed out hereafter. Admitting the atomic hypothesis of the constitution of matter, it is impossible to conceive of expansion otherwise than as a movement of the molecules of a mass, which has for its effect to increase their mean distance from each other. Hence when heat causes a body to expand, it acts in opposition to the forces which tend to prevent the further separation of the molecules; and the bulk of the body at any given temperature is the result of an equilibrium between these forces and the expansive force of the heat contained in it at that temperature. The forces by which the particles of a mass are held together consist in part of the pressure to which it is subjected from without, and partly of the pressure arising from the mutual attractions of the particles themselves. This latter pressure, which is known as cohesive force, has a much greater effect in determining the bulk of solid and liquid bodies than any pressure which acts upon them from without, and it varies not only in different bodies, but even in the same body its value is different at different temperatures. Hence it is not surprising that the relations subsisting between the temperature and bulk of solid and liquid substances should be somewhat complex. In perfect gases, however, cohesion does not exist, and hence the only opposing force which heat has to overcome in order to cause them to expand is the external pressure. Consequently it is found that the rate of expansion of gases bears a much more simple relation to the heat by which it is caused, than that observed in solid and liquid bodies. It is, therefore, convenient to consider the laws of the expansion of gaseous substances before examining those which regulate the expansion of matter in the two other states of aggregation.

Expansion of Gases.—In a perfect gas, volume, elasticity, and temperature would be related to each other in the manner expressed by the equation

$$pv = J(a + t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

where v is the volume of a given weight of the gas at the temperature t and under the pressure p, and J and a are constants. Hence, if v' were the volume of the same weight of the same gas corresponding to any other pressure, p', and temperature, t', we should have

$$\frac{p\,v}{p'v'} = \frac{a + t}{a + t'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

No absolutely perfect gas, however, is known in nature, so that, according to the best experiments, the values of a which correspond to different values of p, v, and t, are not quite constant, but vary slightly, not only with variations of these factors, but also according to the nature of the gas. The properties of air, however, and the other non-condensable gases accord so nearly with the above formulæ—which are in fact nothing more than a statement of the laws of Boyle and Gay-Lussac (GASES, ii. 819*)—that, except in cases where extreme accuracy is required, the accord may be considered perfect.

If in the above equation (b) we make $p = p'$ we get

$$\frac{1}{a} = \frac{v - v'}{v't - vt'}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

that is, $\frac{1}{a}$ is the *coefficient of expansion of the gas under constant pressure*, or the amount by which that quantity of gas which occupies a unit of volume at 0° C. expands, under constant pressure, when its temperature is raised one degree. Similarly, by making $v = v'$, we have

$$\frac{1}{a} = \frac{p - p'}{p't - pt'}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

or $\frac{1}{a}$ is also the *coefficient of expansion of the gas under constant volume*, or, more correctly (since when $v = v'$ no actual expansion can take place), $\frac{1}{a}$ is the coefficient of increase of elasticity, or the increment of elasticity, under a constant volume, for a rise of temperature of one degree, of a gas whose elasticity at 0° C. is unity. For a perfect gas, it is obvious that these two values of $\frac{1}{a}$ would be equal.

The first tolerably accurate determinations of the coefficients of expansion of gaseous bodies were made by Gay-Lussac. He used in his experiments a vessel shaped much like a thermometer, having a bulb about 1 centimetre in diameter, and a tube about 30 or 40 centimetres long, and 1 or 1·5 millimetres wide. The tube was divided into lengths of equal capacity, and the proportion between the total capacity of the bulb and that of one division of the tube was accurately determined. The apparatus having been filled with air dried by passing through a chloride-of-calcium tube, a drop of mercury, occupying a short length of the divided tube, was employed to cut off the enclosed air from communication with the atmosphere, and at the same time to serve as an index whereby to read off its volume. The bulb was then fixed, with the stem horizontal and projecting through the side, in a vessel filled with water, through the medium of which it could be heated to various temperatures. The volumes occupied by the air at each temperature could be read off upon the divided tube by noting the position of the little column of mercury; but the volumes thus determined required to be corrected (a) for the expansion of the glass, (*b*) for the lower temperature of the portion of air contained in the part of the tube outside the water-bath, and (*c*) for the possible alterations of barometric pressure during the experiment. Independently of these latter alterations, which were always very inconsiderable, the pressure upon the gas remained constant during the experiment: it was the volume which changed. Applying the same method to other gases and to vapours, Gay-Lussac concluded that all gases and vapours (at temperatures sufficiently removed from their points of liquefaction) expanded by heat to the same extent; that, namely, when heated from 0° to 100° C. they expanded in the proportion of 1 : 1·375, or for 1° C. by 0·00375 = $\frac{1}{267}$ of their volume at 0°.

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* Equation (b) may obviously be put into the form $v = v'\,\frac{p'}{p}\cdot\frac{a + t}{a + t'}$, and is then identical with that by which these laws are represented at the place quoted.

The confidence which these results naturally excited, in consequence of the high reputation of the author, was still further increased by the confirmation which they received at the hands of Dulong and Petit, and also because it was considered probable, on theoretical grounds, that in substances in which cohesive force no longer existed, the expansive action of heat should be independent of chemical composition. Hence, when the Swedish physicist Rudberg announced, as the result of his own more accurate experiments, that the coefficient of expansion found by Gay-Lussac was considerably too high, the statement was at first received with hesitation.

Rudberg determined the value of the coefficient of expansion of air $\left(\frac{1}{a}\right)$ between 0° and 100° C. by two series of experiments. In the first he determined the contraction undergone by a given quantity of air on cooling from 100° to 0° under a nearly constant pressure; in the second, the difference in the elastic force at 0° and 100° of a quantity of air kept at the same volume at the two temperatures. Making t and t' in equations (*c*) and (*d*) respectively = 100 and 0, the results of his experiments may be stated as follows:—The mean of twelve experiments by the first method gave for the coefficient of expansion under constant pressure—

$$\frac{1}{a} = \frac{v - v'}{100v'} = 0{\cdot}003648 = \frac{1}{274};$$

the mean of ten experiments by the second method gave for the coefficient of expansion at constant volume—

$$\frac{1}{a} = \frac{p - p'}{100p'} = 0{\cdot}003646 = \frac{1}{274},$$

a result identical with the preceding.

More recently (1841) the expansion of air and other gases has been again made the subject of elaborate experiments by Regnault (*Relation des Expériences . . . . pour déterminer les principales lois et les données numériques qui entrent dans le calcul des Machines à Vapeur*, Mém. Acad. Roy. des Sciences, xxi. 15–120 (1847); also Ann. Ch. Phys. [3] iv. 5 and v. 52) and by Magnus (Pogg. Ann. lv. 1, and lvii. 177).

Regnault made five series of experiments by methods more or less distinct. His first method was the same as the first method employed by Rudberg. It consisted in heating a cylindrical glass vessel of known capacity, about 2·5 or 3 centimetres wide, and about 11 centimetres long, filled with dry air, to 100°; sealing it hermetically at that temperature; then cooling it to 0°, and observing the quantity of mercury which entered on breaking off the point of the instrument under the surface of that metal. The apparatus employed and the method of experimenting were, in fact, exactly the same as in determining a temperature by means of the air-thermometer in the manner already described (pp. 19 and 20): for it is obvious that the same experiment which, the coefficient of expansion of air being known, serves to determine the temperature at which the air-thermometer is sealed, would, if this temperature were known, serve for the determination of the coefficient of expansion.

The second set of determinations were made by a method only slightly different from the first, the only essential difference in the apparatus being that the tube connected with the air-reservoir was about 40 centimetres (16 inches) long, and that a portion of it, about two inches long and separated from the air-reservoir by about four inches, was wide enough to produce only a very slight capillary depression in a column of mercury. The effect of this modification of the apparatus was that when, after being heated to 100° and sealed at that temperature, the instrument was placed with the tube pointing vertically downwards and with the point dipping into mercury, the mercury rose only as far as the wide part of the tube, on breaking off the point, and did not reach the reservoir at all. Hence the space occupied by the air at zero differed from that which it had occupied at 100°, only by the capacity of that portion of the tube which became filled with mercury on opening the point; and since the diameter of the tube was, with the exception of the wider portion already mentioned, very small, this capacity bore a small proportion to the total capacity of the instrument. The experiment consisted therefore essentially in a determination of the difference of the elastic force of the air at the two temperatures.

In the third and fourth sets of experiments, the air-reservoir was made to communicate with a manometer, whereby the pressure upon the enclosed air could be varied at will and accurately measured. The pressures were so regulated that the air was caused to occupy accurately the same volume at 0° and 100°, and the differences of pressure required were determined. The apparatus for the third series of experiments was copied, with some improvements of detail, from that employed by Rudberg in his second series. The apparatus for the fourth series was the same in principle, but its construction was such that the pressure upon the air could be determined with still greater accuracy than was possible with the preceding apparatus.

In the fifth set of experiments, the pressure upon the air remained constant, and the alteration of volume was determined by weighing the quantity of mercury which filled the space into which it expanded.

The mean results of numerous experiments made by each of these processes were as follows:—If p_0 and v_0 represent respectively the pressure and volume of the air at 0°, and p_1 and v_1 its pressure and volume at 100°, the value of $\frac{p_1 v_1}{p_0 v_0}$ was—

By the first series	1·36623
„ second series	1·36633
„ third series	1·36679
„ fourth series	1·36650
„ fifth series	1·36706

In the second, third, and fourth series, the expansion was calculated from the change of elastic force undergone by the same volume of air when its temperature changed between 0° and 100°; in the experiments made by the first method, both pressure and volume changed considerably, so that they gave a mixed result. From the consideration of all the experiments by the first four methods, Regnault adopts for the coefficient of expansion of air, under *constant volume*, for 1 degree centigrade between 0° and 100°, the number

$$0·003665 = \frac{1}{272·9} = \frac{1}{273} \text{ nearly.*}$$

This result agrees precisely with that obtained by Magnus.

For the coefficient of expansion of air under *constant pressure*, Regnault adopts the number

0·00367

given by the experiments of the fifth series.

Similar experiments extended to other gases gave the mean results recorded in the following table, in which are also included the results obtained by Magnus:—

Table of Expansion of Gases *between* 0° *and* 100° *at Ordinary Pressures.*

Name of gas.	Value of $\frac{p_1 v_1}{p_0 v_0} = 1 + \frac{100}{a}$.		
	Constant volume.		Constant pressure.
	Regnault.	Magnus.	Regnault.
Hydrogen . . .	1·3667	1·3657	1·3661
Air	1·3665	1·3665	1·3670
Nitrogen . . .	1·3668		
Carbonic oxide . .	1·3667	. .	1·3669
Carbonic anhydride .	1·3688	1·3691	1·3710
Nitrous oxide . .	1·3676	. .	1·3719
Sulphurous anhydride .	1·3845	1·3856	1·3903
Cyanogen . . .	1·3829	. .	1·3877

The foregoing results are all deduced from experiments in which the gases operated upon were subject to pressures differing but little from the ordinary pressure of the atmosphere. In another investigation (*Op. cit.* pp. 96–120) Regnault determined the coefficients of expansion of air and some other gases at pressures considerably different from that of the atmosphere. The following table gives the mean results:

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* If the coefficient of expansion of air be taken = 0·0036666 . . . . it may be represented by the vulgar fraction $\frac{11}{3000}$, a number which is very convenient for the purposes of calculation.

Table of Expansion of Gases *between* 0° *and* 100° *at Various Pressures.*

Air.

Constant Volume.		*Constant Pressure.*	
Density. (Density of air at 0° and 760 mm. pressure = 1.)	$\frac{p_1}{p_0} = 1 + \frac{100}{a}$.	Pressure. mm.	$\frac{v_1}{v_0} = 1 + \frac{100}{a}$.
0·1444	1·36482	760	1·36706
0·4937	1·36572	2525	1·36944
1·0000	1·36650	2620	1·36964
2·2084	1·36760		
2·8213	1·36894		
4·8100	1·37091		

Carbonic Anhydride.

Constant Volume.		*Constant Pressure.*	
Density. (Density of carbonic anhydride at 0° and 760 mm. pressure = 1.)	$\frac{p_1}{p_0} = 1 + \frac{100}{a}$.	Pressure. mm.	$\frac{v_1}{v_0} = 1 + \frac{100}{a}$.
1·0000	1·36856	760	1·37099
1·1879	1·36943	2520	1·38455
2·2976	1·37523		
4·7318	1·38598		

Hydrogen.

Constant Pressure.	
Pressure. mm.	$\frac{v_1}{v_0} = 1 + \frac{100}{a}$.
760	1·36613
2545	1·36616

Sulphurous Anhydride.

Constant Pressure.	
Pressure. mm.	$\frac{v_1}{v_0} = 1 + \frac{100}{a}$.
760	1·3903
985	1·3984

The following general conclusions may be drawn from these results:

1°. The coefficients of expansion of air, hydrogen, nitrogen, and carbonic oxide, between 0° and 100°, are sensibly equal.

2°. The coefficients of expansion of the condensable gases, carbonic anhydride, nitrous oxide, sulphurous anhydride, and cyanogen, are slightly greater than the coefficient of expansion of the permanent gases. For the condensable gases also the coefficient of expansion (under constant pressure) slightly exceeds the coefficient of increase of elasticity (the gas being kept at constant volume), a difference which is likewise observed, though in a less degree, in the case of air.

3°. The coefficient for hydrogen is not influenced by a change of pressure from 1 to 3 atmospheres. The coefficients for air, carbonic anhydride, and sulphurous anhydride are greater at high densities and pressures than at low ones.

Notwithstanding the differences in the absolute values of the coefficients of expansion of air at different densities, and of air, hydrogen, and carbonic anhydride, Regnault found by direct experiments (*Op. cit.* pp. 171–190) that the elastic force of air, of any initial pressure at 0° between 400 mm. and 1300 mm., and the elastic force of hydrogen and carbonic anhydride increased according to the same law at all temperatures between 0° and 350° C. Hence gas-thermometers filled with air of any density, or with hydrogen, or carbonic anhydride, would give perfectly similar indications, provided that, in calculating the temperatures, the coefficient proper to each gas were employed. The coefficient of expansion of sulphurous anhydride was found to diminish, relatively to that of air, in proportion as the temperature rose, being 0·0038251 at 98·12° of the air-thermometer, and 0·0037893 at 310·31°.

Hence as a general conclusion: Although no gas appears to follow *absolutely* the law of expansion expressed by the equations (a) and (b), page 45, the permanent gases follow this law so closely that, in all except the most refined calculations, these formulæ may be taken as strictly applicable to them, the value of a being for all a number sensibly equal to 273.

The following consequences of these equations are of importance in calculating the changes of volume and elastic force of gases corresponding to given changes of temperature: Let v be the volume of a given weight of gas at 0° C., and p its elastic force at the same temperature; let v_1 and p_1 be the volume and elastic force of the same quantity of gas at any other temperature, t_1°; and let v_2 and p_2 be the volume and elastic force corresponding to any third temperature, t_2°: then, the volume at t_1, expressed in terms of the volume at 0°, will be—

$$v_1 = v\frac{p}{p_1}\cdot\frac{a+t_1}{a} = v\frac{p}{p_1}\cdot\left(1+\frac{1}{a}t_1\right),$$

or

$$v_1 = v\frac{p}{p_1}\cdot\frac{273+t_1}{273} = v\frac{p}{p_1}\cdot\left(1+\frac{1}{273}t_1\right) = v\frac{p}{p_1}\cdot\left(1+0{\cdot}003665\,t_1\right);$$

the volume at 0°, in terms of the volume at t_1°, will be—

$$v = v_1\frac{p_1}{p}\cdot\frac{a}{a+t_1} = v_1\frac{p_1}{p}\cdot\frac{1}{1+\frac{1}{a}t_1},$$

or

$$v = v_1\frac{p_1}{p}\cdot\frac{273}{273+t_1} = v_1\frac{p_1}{p}\cdot\frac{1}{1+\frac{1}{273}t_1} = v_1\frac{p_1}{p}\cdot\frac{1}{1+0{\cdot}003665\,t}$$

and the volume at t_2°, in terms of the volume at t_1°, will be—

$$v_2 = v_1\frac{p_1}{p_2}\cdot\frac{a+t_2}{a+t_1} = v_1\frac{p_1}{p_2}\cdot\frac{1+\frac{1}{a}t_2}{1+\frac{1}{a}t_1},$$

or

$$v_2 = v_1\frac{p_1}{p_2}\cdot\frac{273+t_2}{273+t_1} = v_1\frac{p_1}{p_2}\cdot\frac{1+0{\cdot}003665\,t_2}{1+0{\cdot}003665\,t_1}.$$

The elastic force at t_1°, in terms of the elastic force at 0°, will be—

$$p_1 = p\frac{v}{v_1}\cdot\frac{a+t_1}{a} = p\frac{v}{v_1}\cdot\left(1+\frac{1}{a}t_1\right),$$

or

$$p_1 = p\frac{v}{v_1}\cdot\frac{273+t_1}{273} = p\frac{v}{v_1}\cdot\left(1+\frac{1}{273}t_1\right) = p\frac{v}{v_1}\cdot\left(1+0{\cdot}003665\,t_1\right);$$

the elastic force at 0°, in terms of the elastic force at t_1°, will be—

$$p = p_1\frac{v_1}{v}\cdot\frac{a}{a+t_1} = p_1\frac{v_1}{v}\cdot\frac{1}{1+\frac{1}{a}t_1},$$

or

$$p = p_1\frac{v_1}{v}\cdot\frac{273}{273+t_1} = p_1\frac{v_1}{v}\cdot\frac{1}{1+\frac{1}{273}t_1} = p_1\frac{v_1}{v}\cdot\frac{1}{1+0{\cdot}003665\,t_1};$$

and the elastic force at t_2°, in terms of the elastic force at t_1°, will be—

$$p_2 = p_1\frac{v_1}{v_2}\cdot\frac{a+t_2}{a+t_1} = p_1\frac{v_1}{v_2}\cdot\frac{1+\frac{1}{a}t_2}{1+\frac{1}{a}t_1},$$

or

$$p_2 = p_1\frac{v_1}{v_2}\cdot\frac{273+t_2}{273+t_1}\cdot = p_1\frac{v_1}{v_2}\cdot\frac{1+0{\cdot}003665\,t_2}{1+0{\cdot}003665\,t_1}.$$

It is very important to bear in mind, with reference to all calculations of this kind, that when the coefficient of expansion of the permanent gases is said to be uniform at all temperatures, and equal to $\frac{1}{273}$, it is not meant that 1 vol. of a gas at any temperature, t_1°, becomes $1\frac{1}{273}$ vol. at the temperature $(t+1)^\circ$; but that 1 vol. at 0° becomes $1\frac{1}{273}$ vol. at 1°, and $1+\frac{t}{273}$ vol. at t°, and that consequently 1 vol. at t° becomes $1+\frac{1}{273+t}$ at $(t+1)^\circ$.

The irregularities in the expansion of the more condensable gases, particularly sulphurous anhydride, which are brought to light by Regnault's experiments, are met with to a greater or less extent in the case of all liquefiable gases or vapours, and are more marked in proportion as the gases are examined nearer to their points of liquefaction. The law with regard to the expansion of vapours appears to be, that their coefficients of expansion are considerably greater than $\frac{1}{273}$ at temperatures near to the boiling points of the liquids from which they are formed, and that they continue to diminish as the temperature rises, so as to approach more and more closely to a constant value of nearly $\frac{1}{273}$. Hence, at sufficiently high temperatures, all vapours and liquefiable gases acquire the properties of sensibly perfect gases. The rapidity with which the coefficients of expansion of different vapours approach their limiting values, varies greatly. Some vapours, as that of ether, have a nearly uniform rate of expansion within twenty or thirty degrees of the boiling point of the liquid, whereas others show a sensibly diminishing rate of expansion throughout a much wider interval of temperature: for instance, acetic acid through upwards of 120 degrees, and sulphur-vapour through 400 degrees above the boiling point of sulphur. This property of vapours is of great importance in relation to the experimental determination of their densities. (For further details, see SPECIFIC GRAVITY; also ii. 811.) The fact of a vapour having reached a temperature at which its rate of expansion is the same as that of air, is indicated by its density, compared with that of air at the same temperature and pressure, remaining constant for any further rise of temperature: thus the density of acetic acid vapour (boiling point 118°) was found, by Cahours, to be,

at	125°,	150°,	180°,	200°,	240°,	270°,	310°,	336° C.,
=	3·180,	2·727,	2·438,	2·248,	2·090,	2·088,	2·085,	2 083.

That is to say, it expands more rapidly than air up to about 240°, but above that temperature its expansion is very nearly the same as that of air.

Relation between the Expansion of a perfect Gas and the Quantity of Heat required to produce it.—Equation (a) (page 45) may be written—

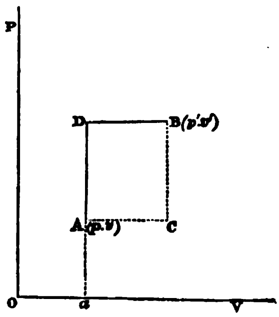
$$p\,v = m\,(1 + a\,t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (e)$$

if we put m for Ja, and a for $\frac{1}{a}$ = coefficient of expansion. Let the volume, v, be expressed in cubic metres, the pressure, p, in kilogrammes per square metre, and the temperature, t, in degrees of the centigrade thermometer. Then, since m is a constant, its value is independent of the variations of v, p, and t, and in order to find it, we may make any suppositions we please with regard to these factors. To determine its value, let p be the normal atmospheric pressure of 0·76 metre referred to 1 square metre, = 10,333 kilogr., let v be one cubic metre, and let t be 0° C. Then we see that m must be the atmospheric pressure on 1 square metre = 10,333 kilogr. = H, and we have—

$$p\,v = H(1 + a\,t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (f)$$

In *fig.* 533 let distances measured parallel to the axis of abscissæ, OV, represent volumes, and distances measured parallel to the axis of ordinates, OP, represent pressures. Then, since the condition of a gas is defined if p and v, two of the three variable quantities upon which it depends, are known, that condition may be represented by the position of a point relatively to the lines OP and OV. Let the point A represent the initial condition ($p \,.\, v$) of a gas: we will consider the quantities of heat which must be imparted to, or withdrawn from, the gas, in order to make it pass through the series of conditions represented by the sides of the rectangle ADBCA, parallel to OP and OV.

Fig. 533.



1. When the gas passes from the state A to the state D, its elastic force increases while its volume, v, remains unaltered; to produce this change, its temperature must be raised from t to the temperature t_1 which is given by the equation $p'\,v = H(1 + a\,t_1)$, which, combined with (f), $pv = H(1 + a\,t)$, gives $(p' - p)\,v = H\,a\,(t_1 - t)$. Hence, putting D for the weight of a cubic metre of the gas at 0°, and c for its specific heat when kept at a constant volume, we have for the quantity of heat which must be imparted to the gas to produce the change in question, the expression—

$$q = Dc\,(t_1 - t);$$

but, by the last equation, $t_1 - t = v\frac{p' - p}{H\alpha}$, therefore—

$$q = \frac{D}{H\alpha} c\, v\, (p' - p) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (g)$$

2. When the gas passes from the condition D to the condition B, it remains under the constant pressure p', but its volume increases from v to v': its temperature must therefore be still further raised to t', which is given by the formula $p'v' = H(1 + \alpha t')$. This, combined with $p'v = H(1 + \alpha t_1)$, gives $p'(v' - v) = H\alpha(t' - t_1)$; hence the quantity of heat required will be $q_1 = Dc'(t' - t_1)$, c' denoting the specific heat under constant pressure. Putting for $t' - t_1$ its value deduced from the previous equation, this becomes—

$$q_1 = \frac{D}{H\alpha} c' p' (v' - v) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (h)$$

3. In passing from the condition B to the condition C, the gas is cooled without change of volume; the corresponding temperature t_2 is therefore given by the formula $pv' = H(1 + \alpha t_2)$, which, combined with $p'v' = H(1 + \alpha t')$, gives $(p' - p)v' = H\alpha(t' - t_2)$. The heat that must be withdrawn will therefore be $q' = Dc(t' - t_2)$, or, by substitution—

$$q' = \frac{D}{H\alpha} c\, v' (p' - p) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (i)$$

4. Lastly, when the gas passes from the condition C to its original condition A, it cools under the constant pressure p, and its temperature again becomes t, defined by the formula $pv = H(1 + \alpha t)$, which, combined with $pv' = H(1 + \alpha t_2)$, gives $p(v' - v) = H\alpha(t_2 - t)$. The quantity of heat to be withdrawn, to cause the temperature to fall from t_2 to t, will be $q'_1 = Dc'(t_2 - t)$, which, by substitution, becomes—

$$q'_1 = \frac{D}{H\alpha} c' p (v' - v) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (k)$$

The general result is that, during the passage of the gas from the state A to the state B, a quantity of heat is expended which (by g and h) is represented by—

$$Q = q + q_1 = \frac{D}{H\alpha}\left[c\, v (p' - p) + c' p' (v' - v)\right]; \quad . \; . \; . \; . \quad (l)$$

and that, during the return of the gas from the condition B to the condition A, a quantity of heat is evolved, which (by i and k) is expressed by—

$$Q' = q' + q_1' = \frac{D}{H\alpha}\left[c\, v' (p' - p) + c' p (v' - v)\right]. \quad . \; . \; . \; . \quad (m)$$

Consequently, there is an ultimate expenditure of a quantity of heat equal to—

$$Q - Q' = \frac{D}{H\alpha}(c' - c)(p' - p)(v' - v),$$

a quantity which is necessarily positive, so long as $p' - p$ and $v' - v$ are positive (that is, so long as any actual increase of pressure and volume takes place), being proportional to the product of these two quantities, and is represented by the area of the rectangle ADBCA.

By tracing in the same way the heat expended and evolved in the cycle of changes represented by the passage of the point A about the same rectangle, but in the opposite direction, ACBDA, it would be found that, as a final result, a quantity of heat $= Q - Q'$ would be *evolved* by the process instead of expended. Hence we see that the quantity of heat necessary to change the condition of a gas from A $(p \,.\, v)$ to B $(p' \,.\, v')$, depends not only on the nature of the conditions A and B, but also on the manner in which the passage from one to the other takes place.

If B approaches indefinitely near to A, the quantity of heat, $Q - Q'$, expended or evolved as the point A passes round the rectangular circuit approaches indefinitely to the value 0. That is, in order to cause a gas to pass from the condition A to the condition B, infinitely near to it, the same infinitely small quantity of heat must be expended whether the passage is in the direction ADB, the direction ACB, or that of the diameter of the rectangle, AB. Hence, an element, AB, of any curve may be replaced by its two projections DA and DB parallel to the axes, and changes of condition represented by curve-lines may be considered as made up of rectangular elements parallel to these axes, so that the result derived from the consideration of the rectangular circuit ADBCA may be extended to a closed circuit of any form whatever. (Bourget, Ann. Ch. Phys. [3] lvi. 257; also Daguin's *Traité de Physique*, 2nd ed. ii. 512.—See further the section of this article: Relations of Heat to Mechanical Energy.)

Attention must here be drawn to an important consequence of the relations that we have found to exist between the pressure, volume, and temperature of a gas. The consequence referred to will be most easily deduced from the above equations (h) and (k), which show that, when a gas expands from the volume v to the volume v', under the constant pressure p, a quantity of heat is absorbed equal to

$$q = \frac{D}{H\alpha} c' p (v' - v),$$

and that when the gas contracts from the volume v' to the volume v, under the same pressure, an equal quantity of heat is evolved. It is plain, however, from the above equation, that if p, the pressure upon the gas, is nothing, the quantity of heat, q, needed to cause the gas to expand will also be nothing. This condition is actually fulfilled when, instead of having to force up a piston or overcome the pressure of the atmosphere in its expansion, a gas is allowed to expand into a vacuous space; and it has been experimentally proved by Joule that the expansion of a gas, under these circumstances, is not attended with expenditure or absorption of heat. He immersed two copper vessels in water, and removed the air from one and compressed an additional quantity of air into the other, until the pressure amounted to 22 atmospheres: on opening a communication between the two, air rushed from the latter vessel into the exhausted one until the pressure in both was 11 atmospheres. Nevertheless, the water by which they were surrounded indicated no alteration of temperature.

Absolute Zero of Temperature.—It results from the fundamental formula of gaseous expansion,

$$p v = J(a + t),$$

that, if the temperature, t, of a gas were reduced until it became $= -a = -273$, the gas would cease to have any gaseous elasticity—the product of elastic force into volume would be $= 0$. The temperature $-273°$ C. is therefore called the **absolute zero** of temperature, and temperatures reckoned from it are called **absolute temperatures**. These are obviously obtained in any case by adding 273 to the number of degrees by which a temperature is expressed on the centigrade scale; and by employing them in the expression of the laws regulating the relations between temperature and other properties, the resulting expressions are often much simpler than those required when temperatures are expressed according to any ordinary thermometric scale. Thus, for instance, by using τ ($= t + 273$) to denote the absolute temperature corresponding to the centigrade temperature t, we have for the fundamental formulæ (a) and (b) (page 45) relating to pressure, volume, and temperature, the expressions

$$p v = J\tau \text{ and } \frac{p' v'}{p v} = \frac{\tau'}{\tau},$$

and corresponding simplifications will be found to result in many other cases.

Expansion of Liquids.—The relation between the volume of a given weight of liquid and its temperature follows no simple general law, such as that which, as we have seen, applies, at least approximately, in the case of gases. On the other hand, not only has almost every liquid a coefficient of expansion different from that of any other, but the coefficient of the same liquid varies to an important extent with changes of temperature.

In consequence of the small extent to which the volume of liquid substances is influenced by external pressure (ELASTICITY, ii. 370), it may, in all ordinary cases, be considered as a function of their temperature alone, instead of as a function of temperature and pressure combined, as with gases. It results also from the cohesion of liquids, which causes them always to have a definite limiting surface, that their volumes can be determined by observations of a more direct kind than those which can be made on gaseous bodies. Hence, an obvious method of determining the expansion of a liquid, is to observe how many divisions of a vessel graduated into parts of equal capacity, are filled by the same weight of it at various temperatures. Such a method, however, would only be exact if the capacity of the containing vessel were known, not merely at some one temperature, but at each temperature at which an observation of the liquid was made. Thus, it would be inaccurate to conclude that the expansion of a liquid between 0° and 100° amounted to 1 per cent., because the same quantity which filled 100 divisions at the former temperature occupied 101 divisions at the latter; for it is impossible to raise the temperature of a liquid, without at the same time raising the temperature, and so altering the capacity, of the vessel in which it is contained. It is therefore necessary to distinguish between the *apparent* expansion of liquids, or that which would result from observations made in the manner that has been described, without taking account of the changes of capacity of the containing vessel, and their *real* or *absolute* expansion, which is the apparent expansion corrected for the simultaneous expansion of the vessel. Of course, in measuring the changes of volume of gaseous bodies, the expansion of the containing vessel requires to be similarly taken into account, but in this case it is of much less relative consequence than it is in the case of liquids: thus, for example, the apparent expansion of air in a glass vessel would only differ from its real expansion about in the proportion of 140 : 141; whereas, in the case of mercury, the difference would amount to one seventh of the total effect to be observed.

Relation between the Absolute and Apparent Expansion of Liquids.—From what has been already said, it will be evident that the apparent expansion of a liquid is equal to its absolute expansion for the same interval of temperature diminished by the corresponding expansion of the containing vessel. That is, if Δ be the coefficient of absolute expansion of a liquid, and δ its coefficient of apparent expansion, the relation between these two quantities will be the following:—Let V be the volume of the liquid, and consequently of that portion of the vessel which it fills, at 0°; and let V' be the capacity, *estimated at* 0°, of so much of the vessel as it fills when its temperature has been raised 1°. Then the real volume of the liquid at the latter temperature will be $V(1 + \Delta)$, and the real volume of the portion of the vessel occupied by it will be $V'(1 + \kappa)$ (putting κ for the coefficient of cubical expansion of the material of the vessel): hence we have—

$$V'(1 + \kappa) = V(1 + \Delta),$$

or

$$\frac{V' - V}{V} = \frac{\Delta - \kappa}{1 + \kappa};$$

but $V' - V$ is the apparent increase of volume of the liquid, for a rise of temperature of one degree; $\frac{V' - V}{V}$ is therefore its coefficient of apparent expansion $= \delta$. Accordingly—

$$\delta = \frac{\Delta - \kappa}{1 + \kappa}, \text{ or } \Delta = \delta + \kappa + \delta\kappa;$$

but as δ and κ are always small fractions, we may disregard their product, $\delta\kappa$, and put $\Delta = \delta + \kappa$: that is, the *coefficient of absolute expansion of a liquid is equal to its coefficient of apparent expansion in a vessel of any material, together with the coefficient of cubical expansion of the material of which the vessel is made.*

By far the most accurate method of measuring the capacity of a vessel, and of finding the relative values of divisions which may be marked upon it, is to determine the weight of mercury which fills it up to the zero point of the scale, and also the weight which corresponds to the interval between any two divisions. But since both the capacity of the vessel and the specific gravity of mercury vary with variations of temperature, the different weights of mercury which fill the vessel at different temperatures do not at once enable its relative capacities at these temperatures to be calculated; for this it is necessary that the absolute expansion of mercury should be previously known. Hence the absolute expansion of mercury (which, on account of its inalterability and its property of not wetting glass, is better adapted for measuring purposes than any other liquid) is a necessary preliminary datum for the determination of the absolute expansion of liquids in general.

Determination of the Absolute Expansion of Mercury.—Enough has already been said to make it evident that, in order to obtain a trustworthy determination of this constant, some method must be devised whose results are wholly unaffected by changes in the capacity of the vessel in which the mercury is contained. A satisfactory solution of this apparently very difficult problem was first given by Dulong and Petit (Ann. Ch. Phys. [2] vii. 124 (1817); Daguin's *Traité de Physique*, 2nd ed. ii. 187; see also Regnault, *Relation des Expériences, &c.*, pp. 277–280. Paris, 1847). Their method consisted in measuring the heights of columns of mercury at different temperatures, which produced equilibrium with another column of the same liquid of constant height, and kept always at 0°.

If h denotes the height of the column at 0°, d the density of mercury at this same temperature, h' the height of the column at t°, which produces equilibrium with the first, and d' the density of mercury at the temperature t, we have—

$$\frac{h'}{h} = \frac{d}{d'}.$$

Representing by v and v' the volumes of the same weight of mercury at 0° and at t°, we get—

$$\frac{d}{d'} = \frac{v'}{v}, \text{ and consequently } \frac{v'}{v} = \frac{h'}{h}.$$

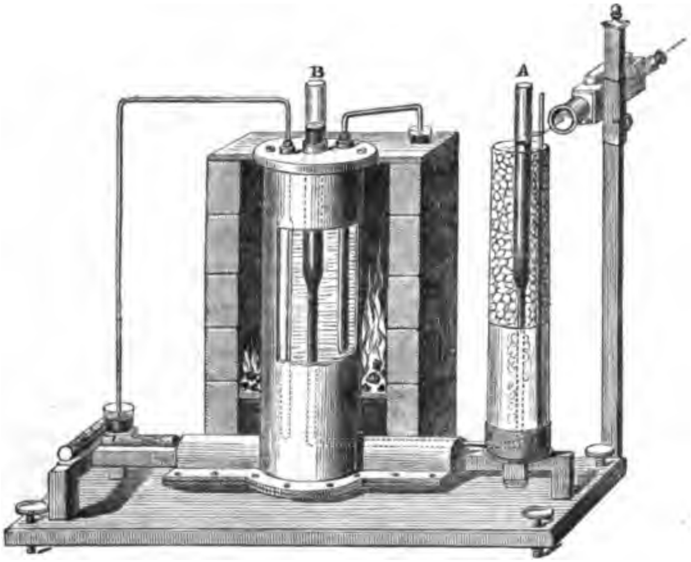
The mean coefficient of expansion between 0° and t° is therefore—

$$\delta_t = \frac{v' - v}{v} = \frac{h' - h}{h},$$

and its determination requires only that the difference of height of the two columns, and the absolute height of the column at zero, should be accurately measured.

The apparatus employed by Dulong and Petit for the purpose of putting this method into practice is represented in *fig.* 534. It consisted of a kind of inverted glass syphon, the two vertical branches of which (A and B) were about 0·55 metre long, and communicated below by a horizontal tube of very small diameter. The branch A was surrounded by a cylinder of tinned iron which was kept full of ice; the other branch, B, occupied the middle of a cylindrical copper vessel filled with oil and built into a furnace.

Fig. 534.



(In the figure, the front wall of the furnace, as well as a part of the cylinders surrounding each branch of the syphon, is represented as having been removed.) The quantity of mercury in the apparatus was so adjusted that the meniscus in the tube B was a little above the cover of the oil-bath, and the difference in the height of the two columns was measured by a cathetometer (an instrument devised by Dulong and Petit, and first used in this investigation). The temperature of the oil-bath was indicated by an air-thermometer and a mercurial weight-thermometer (pp. 18, 19), the reservoirs of which were of the same length as the mercury-column in the tube B, and were placed near to and parallel with it.

The following table gives the general results of a great number of determinations made with this apparatus:

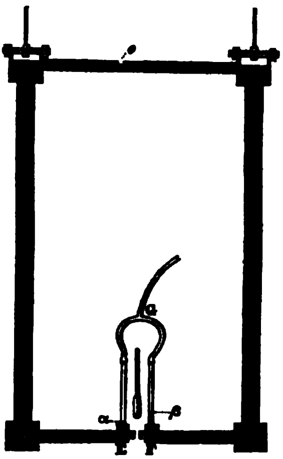
Absolute Expansion of Mercury (Dulong and Petit).

Temperatures by the air-thermometer.	Mean coefficient of Expansion counted from 0°.			
	Maximum values.	Minimum values.	Mean values.	
100° C. . .	$\frac{1}{5547}$	$\frac{1}{5552}$	$\frac{1}{5550}$	= 0·00018018
200° . . .	$\frac{1}{5419}$	$\frac{1}{5431}$	$\frac{1}{5425}$	= ·00018433
300° . . .	$\frac{1}{5289}$	$\frac{1}{5309}$	$\frac{1}{5300}$	= ·00018868

Notwithstanding the great approach to accuracy which was undoubtedly made in these experiments, the results were still affected by sources of error which, in the determination of a physical constant of such primary importance as the one in question, cannot be considered as immaterial. The chief of these are: the uncertainty of the determinations of the temperature of the heated column, arising (1) from the employment of the old (and inaccurate) coefficient for the expansion of air, namely 0·00375, in reducing the indications of the air-thermometer; (2) the cooling effect of the external air upon the portion of the heated column which rose above the cover of the oil-bath; (3) the want of uniformity in the temperature of the oil-bath at different depths; and the comparative shortness of the two mercury-columns, whereby a very small absolute error in the measurement of h and h' comes to have a considerable effect on the value of the fraction $\frac{h' - h}{h} = \delta$.

In order to obtain results which should be, as far as possible, free from the errors thus arising, Regnault (*Relation des Expériences, &c.*, pp. 271–328. Paris, 1847) repeated the determination of the absolute expansion of mercury, by a method similar in principle to that of Dulong and Petit, but somewhat different in execution. The arrangement of his apparatus will be intelligible from *fig.* 535. AB and CD are two iron tubes, 1·5 metre long and 10 mm. in internal diameter (in the figure the diameter is greatly exaggerated in proportion to the length), connected above by the horizontal iron tube AC, of 2·5 mm. (0·1 inch) internal diameter, and respectively communicating below with the horizontal tubes BE and DF, likewise of 2·5 mm. diameter, which in their turn carry the vertical glass tubes EG and FG. The apparatus having been adjusted so that the tubes AB and CD are exactly vertical, and the tubes AC, BE, and DF exactly horizontal, mercury is poured into it through one of the short tubes, open at both ends, by which both AB and CD are surmounted, and in proportion as the liquid rises in the glass tubes EG and FG, air is compressed into a copper receiver communicating with them by the leaden pipe G, so as to keep the level of the mercury near the bottom of the glass tubes. The addition of mercury is continued until it begins to run out at a hole, O, bored in the upper side of the tube AC. The vertical tube AB is placed in the centre of an oil-bath; CD is surrounded by a constant current of cold water.

Fig. 535.



On heating the tube AB, the density of the mercury contained in it was of course diminished, and consequently equilibrium of pressure in the tubes EG and FG could only be maintained by the sinking of the mercury-column in the former. The elastic force of the compressed air in the receiver was therefore balanced—on the one hand, by the pressure of the heated column of mercury of the height AB, $= H$, diminished by that of the column in E, $= h$; on the other hand, by the pressure of the cold column CD, $= H'$, diminished by that of the column in F, $= h'$. The temperature of the column AB was indicated by an air-thermometer, that of CD by three mercurial thermometers in the water-vessel which surrounded it, and that of the mercury in E and F by a thermometer placed between them as shown in the figure. When the necessary corrections for the differences of temperature of the several mercury-columns had been applied, the formula for the absolute expansion became—

$$\frac{(H' - h') - (H - h)}{H' - h'} = \delta.$$

But since the required corrections involved the knowledge of the very coefficient sought, the calculation could only be made by the method of successive approximations: that is, Dulong and Petit's coefficient was first assumed in order to calculate an approximate result; then the number so obtained was substituted for the old coefficient, and so a still more accurate result was arrived at.

In another series of experiments, the tubes AB and CD were connected at the bottom by a continuous horizontal tube, and the tube AC was cut across, vertical glass tubes being inserted into the two halves, wherein the different heights attained by the mercury-columns could be observed. In this state, the apparatus was merely a modified form of that employed by Dulong and Petit.

The results ultimately arrived at are given in the following table, the temperatures in the first column of which are those measured by the air-thermometer.

The numbers in the last column of this table represent the amounts by which a unit volume of mercury expands for a rise of temperature of one degree centigrade at various temperatures between 0° and 350°. Thus, 100,000,000 cubic millimetres of mercury, measured at 0°, occupy 100,017,905 cubic millimetres at 1°; 100,000,000 cubic milli-

Absolute Expansion of Mercury (Regnault).

Temperature = t.	Volume at $t°$.	Mean coefficient of expansion between 0° and $t°$.	True coefficient of expansion at $t°$.
0°	1·000000	0·00000000	0·00017905
10	1·001792	0·00017925	0·00017950
20	1·003590	0·00017951	0·00018001
30	1·005393	0·00017976	0·00018051
40	1·007201	0·00018002	0·00018102
50	1·009013	0·00018027	0·00018152
60	1·010831	0·00018052	0·00018203
70	1·012655	0·00018078	0·00018253
80	1·014482	0·00018102	0·00018304
90	1·016315	0·00018128	0·00018354
100	1·018153	0·00018153	0·00018405[*]
110	1·019996	0·00018178	0·00018455
120	1·021844	0·00018203	0·00018505
130	1·023697	0·00018228	0·00018556
140	1·025555	0·00018254	0·00018606
150	1·027419	0·00018279	0·00018657
160	1·029287	0·00018304	0·00018707
170	1·031160	0·00018329	0·00018758
180	1·033039	0·00018355	0·00018808
190	1·034922	0·00018380	0·00018859
200	1·036811	0·00018405	0·00018909
210	1·038704	0·00018430	0·00018959
220	1·040603	0·00018456	0·00019010
230	1·042506	0·00018481	0·00019061
240	1·044415	0·00018506	0·00019111
250	1·046329	0·00018531	0·00019161
260	1·048247	0·00018557	0·00019212
270	1·050171	0·00018582	0·00019262
280	1·052100	0·00018607	0·00019313
290	1·054034	0·00018632	0·00019363
300	1·055973	0·00018658	0·00019413
310	1·057917	0·00018683	0·00019464
320	1·059866	0·00018708	0·00019515
330	1·061820	0·00018733	0·00019565
340	1·063778	0·00018758	0·00019616
350	1·065743	0·00018784	0·00019666

metres, measured at 300°, become 100,019,413 cubic millimetres at 301°. Accordingly, the true coefficient of expansion increases as the temperature rises. The third column contains the quotients obtained by dividing the difference between the volume (V_t) of mercury at $t°$ and the volume of the same weight at 0° ($V_0 = 1$) by the number of degrees of temperature ($= t$), that is to say, the mean coefficient of expansion between 0° and $t°$, $\frac{V_t - 1}{t}$. Between 0° and 100°, the mean coefficients vary so little that the real expansion of mercury, and much more therefore its smaller apparent expansion in glass, may be taken as proportional to the temperature measured by the air-thermometer. A careful comparison of an air-thermometer and a mercurial thermometer, upon which the points 0° and 100° had been determined under the same circumstances, and which therefore necessarily agreed at these temperatures, showed the following differences between the indications of the two instruments:

Temperatures by air-thermometer—

$-$ 36° 0° + 100° 129·9° 148·7° 197·0° 245° 292·7° 350°;

Temperatures by mercurial thermometer—

$-$ 36° 0° + 100° 130° 150° 200° 250° 300° 350°.

From this table it results that if the real expansion of mercury be taken as the measure of temperature, the corresponding temperatures of the air- and mercurial thermometers will be—

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[*] In Regnault's original paper, the true coefficient of expansion at 100° is given, doubtless in consequence of a misprint, as 0·00018305, and the same number is repeated in various other places: *e. g.* Handwörterb. der Chemie, 2nd ed. ii. [1], 567, article *Ausdehnung;* also Daguin's *Traité de Physique*, ii. 193. Paris, 1861.

Air-thermometer—	0°	50°	100°	130°	150°	200°	250°	300°	350°;
Mercurial thermometer—	0°	49·6°	100°	130·5°	151°	202·8°	255·2°	308·3°	362·2°.

By a series of observations of the heights of two mercurial barometers, one of which was kept at a temperature near 0° C., while the other was heated to a higher temperature, **Militzer** (Pogg. Ann. lxxx. 55) obtained for the mean coefficient of absolute expansion of mercury between 0° and 100°, the number

$$0{\cdot}00017405 \pm 0{\cdot}00000082 = \frac{1}{5745{\cdot}4}\left(1 \pm \frac{1}{212}\right),$$

which differs considerably from Regnault's result, and is probably less accurate.

Apparent Expansion of Mercury, and determination of the Cubical Expansion of Glass vessels.—By help of the foregoing table of the absolute expansion of mercury, the cubical expansion of glass vessels may be determined. For this purpose the neck of the vessel is drawn out to a capillary point; it is filled with mercury, care being taken to exclude all moisture or air; exposed successively to the temperatures 0° and 100°, and weighed with the quantity of mercury which fills it at each of these temperatures. Let

the weight of the empty glass vessel be . . . . $= w$,
the weight of the vessel filled with mercury at 0° . . . . . $= W$,
the weight of the vessel filled with mercury at 100° . . . . . $= W'$,

let Δ be the absolute expansion of mercury, and κ the cubical expansion of glass between 0° and 100°; then we have

$$\frac{W - w}{W' - w} = \frac{1 + \Delta}{1 + \kappa}, \text{ and therefore } \kappa = \frac{W' - w}{W - w}(1 + \Delta) - 1.$$

When once the cubical expansion of a glass vessel is known, the absolute expansion of any liquid can be deduced, in the manner already explained (p. 53), from its apparent expansion as observed in this vessel. Hence a problem of frequent occurrence is to determine the expansion of the glass of a vessel shaped like a thermometer, and provided with a divided stem, for which the relative capacities of the bulb and of one division of the stem have been previously determined. In such a case, it is only necessary to fill the apparatus to some particular point of the scale with well-boiled mercury, and to observe the apparent volumes of the mercury, v and v', at 0° and 100°, expressed in divisions of the scale: the expansion of the glass can then be calculated. For (p. 53) the apparent volume of the mercury at 100° is equal to its volume at 0° increased by the amount of its absolute expansion between 0° and 100°; that is:—

$$v'(1 + \kappa) = v(1 + \Delta), \text{ or } \kappa = \frac{v}{v'}(1 + \Delta) - 1.$$

The apparent expansion of mercury in glass varies with the kind of glass employed, but may be taken on an average = 0·0001545 for each degree centigrade. This value may be used, for instance, without hesitation in calculating the corrected length of the portion of the thread of mercury in a thermometer which is not exposed to the temperature that is to be measured. (See below, *Determination of Boiling Points.*) Between 0° and 100° the apparent volume of mercury in glass increases in the proportion of 1 : 1·01545, while the real volume increases in the proportion of 1 : 1·01815; hence the cubical expansion of glass is

$$\kappa = \frac{1{\cdot}01815}{1{\cdot}01545} - 1 = 0{\cdot}002663.$$

Another case in which the absolute expansion of mercury requires to be taken into account, is in reducing barometric observations to 0° C. (BAROMETER, i. 512, 513.)

Expansion of other Liquids.—The absolute expansion of any liquid can now be ascertained by filling with it a small glass bottle, whose cubical expansion has been previously ascertained in the manner already described, and weighing the bottle with the quantity of liquid which fills it at different temperatures. But a more rapid method, and therefore one more frequently adopted, is to observe the apparent expansion of the liquid in a *dilatometer*, an instrument shaped just like a common mercurial-thermometer, and then to correct these observations for the previously known cubical expansion of the glass. In this way very numerous determinations have been made by **Isidore Pierre** (Ann. Ch. Phys. [3] xv. 325; xix. 193; xx. 5; xxi. 336; xxxi. 118; xxxiii. 199) and by **Hermann Kopp** (Pogg. Ann. lxxii. 1 and 223; Ann. Ch. Pharm. xciv. 257; xcv. 307; xcvi. 153 and 303; c. 19). The principal results of these investigations are given below.

Expansion of Water. (Kopp.)

Temperature.	Volume. (Volume at 0° = 1.)	Density. (Density at 0° = 1.)	Volume. (Volume at 4° = 1.)	Density. (Density at 4° = 1.)
0°	1·00000	1·000000	1·00012	0·999877
1	0·99995	1·000053	1·00007	0·999930
2	0·99991	1·000092	1·00003	0·999969
3	0·99989	1·000115	1·00001	0·999992
4	0·99988	1·000123	1·00000	1·000000
5	0·99988	1·000117	1·00001	0·999994
6	0·99990	1·000097	1·00003	0·999973
7	0·99994	1·000062	1·00006	0·999939
8	0·99999	1·000014	1·00011	0·999890
9	1·00005	0·999952	1·00017	0·999829
10	1·00012	0·999876	1·00025	0·999753
11	1·00021	0·999785	1·00034	0·999664
12	1·00031	0·999686	1·00044	0·999562
13	1·00043	0·999572	1·00055	0·999449
14	1·00056	0·999445	1·00068	0·999322
15	1·00070	0·999306	1·00082	0·999183
16	1·00085	0·999155	1·00097	0·999032
17	1·00101	0·998992	1·00113	0·998869
18	1·00118	0·998817	1·00131	0·998695
19	1·00137	0·998631	1·00149	0·998509
20	1·00157	0·998435	1·00169	0·998312
21	1·00178	0·998228	1·00190	0·998104
22	1·00200	0·998010	1·00212	0·997886
23	1·00223	0·997780	1·00235	0·997657
24	1·00247	0·997541	1·00259	0·997419
25	1·00271	0·997293	1·00284	0·997170
26	1·00295	0·997035	1·00310	0·996912
27	1·00319	0·996767	1·00337	0·996644
28	1·00347	0·996489	1·00365	0·996367
29	1·00376	0·996202	1·00393	0·996082
30	1·00406	0·996008	1·00423	0·995787
35	1·00570			
40	1·00753			
45	1·00954			
50	1·01177			
55	1·01410			
60	1·01659			
65	1·01930			
70	1·02225			
75	1·02541			
80	1·02858			
85	1·03189			
90	1·03540			
95	1·03909			
100	1·04299			

The numbers in the second column of the above table, compared with that representing the volume of the same quantity of water at 0°, give the following four interpolation-formulæ—

Between 0° and 25° C.

$$V = 1 - 0{\cdot}000061045\,t + 0{\cdot}0000077183\,t^2 - 0{\cdot}00000003734\,t^3.$$

Between 25° and 50°.

$$V = 1 - 0{\cdot}000065415\,t + 0{\cdot}0000077585\,t^2 - 0{\cdot}000000035408\,t^3.$$

Between 50° and 75°.

$$V = 1 - 0{\cdot}00005916\,t + 0{\cdot}0000031849\,t^2 + 0{\cdot}0000000072848\,t^3.$$

Between 75° and 100°.

$$V = 1 - 0{\cdot}00008645\,t + 0{\cdot}0000031892\,t^2 + 0{\cdot}0000000024487\,t^3.$$

It will be seen that, between 0° and a temperature of about + 4°, water presents the exceedingly rare phenomenon of a substance which contracts when heated and expands when cooled, so that at about 4° it is more dense than at any other temperature. According to the first of the above formulæ, the exact temperature at which water possesses its maximum density would be 4·08°. The results of other experimenters indicate in general very nearly the same temperature for this point. For example, Hällström fixed it at 4·1°, Despretz at 4°, Playfair and Joule at 3·95°, Hagen at 3·87°, Frankenheim at 3·86°, Plücker and Geissler at 3·8° (nearly), C. v. Neumann at 3·68°. Although the melting point of ice (0° C.) is also the point at which water freezes under ordinary circumstances, it may by special precautions be cooled much lower without becoming solid (p. 74). It is then found that the expansion which takes place when water is cooled from 4° to 0°, continues as the temperature sinks below the latter temperature. This is shown in the following table by Despretz (Daguin's *Traité de Physique*, ii. 205. Paris, 1861), which gives the volumes and densities of water for each degree from − 9° to + 4°, compared with its volume and density at 4° as unity. The complete table, which extends from − 9° to 100°, agrees in general very closely with that already given by Kopp; it is therefore not necessary to reproduce it here entire: the portion given corresponds to the last two columns of Kopp's table.

Expansion of Water between − 9° *and* + 4°. (Despretz.)

Temperatures.	Volumes.	Densities.	Temperatures.	Volumes.	Densities.
− 9°	1·0016314	0·998371	− 2°	1·0003077	0·999692
− 8	1·0013734	0·998628	− 1	1·0002138	0·999786
− 7	1·0011354	0·998865	0	1·0001269	0·999873
− 6	1·0009184	0·999082	+ 1	1·0000730	0·999927
− 5	1·0006987	0·999202	2	1·0000331	0·999966
− 4	1·0005619	0·999437	3	1·0000083	0·999999
− 3	1·0004222	0·996577	4	1·0000000	1·000000

Frankenheim (Jahresber. üb. Chemie, u. s. w., 1852, 51) calculated from Pierre's observations the following empirical formulæ, to express the volume of water at t°, compared with its volume at 0° taken as unity:

Between − 13° and 0°.

$$1 - 0{\cdot}00009417\,t + 0{\cdot}000001449\,t^2 - 0{\cdot}0000005985\,t^3.$$

It is not necessary to give the other six similar formulæ which he calculated for other intervals of temperature up to + 98°, nor to reproduce any part of the table which he calculated by means of them, except the following numbers referring to temperatures below 0°:

Temperatures	−15°	−10°	−5°	0°
Volumes .	1·0037584	1·0016851	1·0005819	1·0000000.

Tables of the expansion of water between 0° and 100° have also been constructed by **Hagen** (see Jahresber. üb. Chemie, u. s. w., 1856, 50), **Kremers** (*ibid.* 1861, 62), and others.

Kopp's table further shows that water expands more and more rapidly as the temperature rises. This property likewise is found to remain the same when, by increasing the pressure upon it, water is kept liquid at temperatures above 100°. Thus, for example, by observing under the microscope the apparent expansion of water in thermometer-tubes, **Sorby** (Phil. Mag. [4] xviii. 81) obtained results from which he calculated the following formula for its expansion between 0° and 200°:

$$V = 0{\cdot}9977 + 0{\cdot}000123\,t + 0{\cdot}00000330\,t^2,$$

which accords closely with the formula which he calculated for the same interval of temperature from Kopp's experiments, namely,

$$V = 0{\cdot}997696 + 0{\cdot}0001101\,t + 0{\cdot}00000343\,t^2.$$

Mendelejeff also (Zeitschr. Chem. Pharm. 1861, 33; Ann. Ch. Pharm. cxix. 1) investigated the expansion of water above 100° with the following results:—

Temperatures.	Densities. (Density of water at 4° = 1.)	Volumes. (Volume of water at 0° = 1.)	Volumes calculated by Kopp's formula.
99·8°	0·95908	1·0426	1·0429
131·0	0·93079	1·0722	1·0716
156·8	0·90770	1·1016	1·1014

The presence of saline substances in solution in water renders its rate of expansion more uniform, both below and above 100°. [For determinations of the rate of expansion of aqueous solutions, see **Kremers** (Pogg. Ann. c. 394; Jahresber. üb. Chemie, u. s. w., 1857 [1] 44: chlorides of potassium, sodium, lithium, and barium.—Further, Pogg. Ann. cv. 360; Jahresber. 1858, 41: chlorides of calcium, cadmium, strontium, zinc, magnesium; bromides of potassium, sodium, lithium, barium, strontium.—Further, Pogg. Ann. cviii. 115; Jahresber. 1859, 48: bromides of strontium, calcium, magnesium, zinc, cadmium; iodides of potassium and sodium; hydrochloric acid.—Further, Pogg. Ann. cxi. 60; Jahresber. 1860, 45: iodides of lithium, barium, strontium, calcium, magnesium, zinc, cadmium.—Further, Pogg. Ann. cxiv. 41; Jahresber. 1861, 60: nitrates and sulphates of potassium, sodium, lithium; aqueous nitric and sulphuric acids), **Gerlach** (Jahresber. 1859, 42–48: chlorides of potassium, sodium, lithium, ammonium, magnesium, calcium, barium, aluminium; sulphates of potassium and sodium; carbonates of potassium and sodium; tartaric acid, citric acid, cane-sugar), and **Sorby** (*loc. cit.*: chlorides of potassium and sodium, sulphate of sodium).]

The temperature of maximum density of aqueous solutions is lower than that of pure water. In fact, with solutions of many substances, this temperature lies lower than the ordinary freezing-point of the solution, and is in general (as well as the freezing-point) lower the larger the proportion of saline matter contained in the solution.

Points of Maximum Density and Congelation of Aqueous Solutions. (**Despretz.**)

Substances.	Weight of substance in 997·45 parts of water.	Temperature of maximum density.	Freezing-point of the solution when shaken.
Sea-water . . .	. .	− 3·7°	− 1·88°
Chloride of sodium .	12·3	+ 1·2	− 0·8
" " . .	24·9	− 1·7	− 1·4
" " . .	37·0	− 4·75	− 2·1
" " . .	74·1	− 16·0	− 4·3
Chloride of calcium .	6·2	+ 3·2	− 0·2
" " . .	12·3	+ 2·05	− 0·5
" " . .	24·7	+ 0·06	− 1·0
" " . .	37·0	− 2·4	− 3·9
" " . .	74·1	− 10·4	− 5·3
Sulphate of potassium .	6·2	+ 2·9	− 0·1
" " . .	12·3	+ 1·9	− 0·3
" " . .	24·7	− 0·1	− 0·55
" " . .	37·0	− 2·3	− 2·1
" " . .	74·1	− 8·4	− 4·1
Sulphate of sodium .	6·2	+ 2·5	− 0·2
" " . .	12·3	+ 1·15	− 0·4
" " . .	24·7	− 1·5	− 0·7
" " . .	37·0	− 4·3	− 1·3
Carbonate of potassium .	37·0	− 3·95	− 3·2
" " .	74·1	− 12·4	− 2·25
Carbonate of sodium .	37·1	− 7·0	− 2·85
" " .	74·1	− 17·3	− 2·2
Sulphate of copper .	58·0	− 0·6	− 1·3
Potash	37·4	− 5·6	− 2·1
"	74·1	− 15·95	− 4·3
Alcohol . . .	74·1	+ 2·3	− 2·8
Sulphuric acid . .	12·3	+ 0·6	− 0·4
" " . .	24·7	− 1·9	− 1·1
" " . .	37·0	− 5·0	− 1·3

In the tables which follow, Kopp has collected together the results of his own and Pierre's determinations of the expansion of nearly ninety other liquids, chiefly organic. In each table, the several substances are arranged in the order of their boiling-points, beginning with the lowest. Except where the contrary is stated, the volume of each liquid at 0° C. is taken as the unit, with which its volume at higher temperatures is compared.

Table A (Ann. Ch. Pharm. c. 21) gives the expansion of seven nitrogenous compounds from the determinations of Kopp and Pierre.

Table B (*ibid.* xcvi. 163) gives the expansion of forty-two liquids, containing no other elements than carbon, hydrogen, and oxygen, according to the experiments of H. Kopp:—Table C (*ibid.* xcvi. 304) gives the expansion of thirty-eight compounds containing sulphur, iodine, bromine, and chlorine, according to the experiments of Kopp and Pierre.

TABLE A.

° C.	Kopp.		Pierre.	Kopp.				° C.
	Cyanide of methyl (acetonitrile). C^2H^3N.	Nitrate of ethyl. $C^2H^5NO^3$.	Sulphocyanate of methyl. C^2H^3NS.	Oil of mustard. C^4H^5NS.	Aniline. C^6H^7N.	Cyanide of phenyl (benzonitrile). C^7H^5N.	Nitrobenzene. $C^6H^5NO^2$.	
0	10000	10000	10000	10000	10000	10000	10000	0
10	10122	10117	10098	10107	10083	10093	10084	10
20	10250	10244	10200	10215	10167	10186	10168	20
30	10384	10377	10305	10324	10253	10279	10253	30
40	10523	10517	10416	10434	10342	10373	10340	40
50	10669	10661	10531	10546	10433	10467	10428	50
60	10824	10810	10653	10660	10525	10562	10518	60
70	10988	10962	10781	10777	10619	10659	10609	70
80	11161	11116	10909	10897	10716	10757	10701	80
90		11270	11042	11021	10815	10857	10796	90
100			11178	11148	10915	10961	10892	100
110			11318	11280	11018	11067	10990	110
120			11462	11418	11124	11177	11090	120
130			11609	11561	11231	11289	11192	130
140			11760	11708	11341	11406	11297	140
150				11862	11454	11528	11404	150
160					11569	11652	11512	160
170					11686	11783	11623	170
180					11806	11919	11736	180
190					11928	12061	11853	190
200						12209	11972	200
210							12093	210
220							12218	220

From the inspection of these tables it will be seen that, as a general, though not universal, rule, those substances expand most rapidly at ordinary temperatures whose boiling-points are lowest; that isomeric compounds having the same boiling-point, expand at the same or very nearly the same rate (*e. g.* formate of ethyl and acetate of methyl, $C^3H^6O^2$; propionate of ethyl and butyrate of methyl, $C^5H^{10}O^2$; butyrate of ethyl and valerate of methyl, $C^6H^{12}O^2$); that the rate of expansion of each liquid increases as the temperature rises. This last fact becomes still more apparent on comparing the coefficients of expansion at different temperatures (for a table of the true and mean coefficients of expansion of the liquids examined by Pierre, see Gmelin's *Handbook*, i. 226), and a consequence of it is that, when the volumes of different liquids are compared at the same number of degrees below their several boiling-points, the volume of each liquid at its boiling-point being taken as unity, the alterations corresponding to equal intervals of temperature are found to be often much more uniform than when the comparison is made (as in the tables which follow) for the same absolute temperatures. (Tables of Pierre's results, calculated for equal distances from the boiling-points, are given in Gmelin's *Handbook*, i. 227–230.)

Observations of the expansion of liquids by the methods already described are limited to temperatures below the ordinary boiling-points, but by special methods such observations can be extended to higher temperatures, and it is then found that the increasing rate of expansion continues up to the highest points at which determinations can be made, so that, under such circumstances, liquids may expand as rapidly as

TABLE B.

° C.	Aldehyde. C^2H^4O.	Ether. $C^4H^{10}O$.	Formate of methyl. $C^2H^4O^2$.	Acetate of methyl. $C^3H^6O^2$.	Formate of ethyl. $C^3H^6O^2$.	Acetone. C^3H^6O.	Methylic alcohol. CH^4O.	Acetate of ethyl. $C^4H^8O^2$.	Alcohol. C^2H^6O.	Benzene. C^6H^6.	Butyrate of methyl. $C^5H^{10}O^2$.	Propionate of ethyl. $C^5H^{10}O^2$.	Formic acid. CH^2O^2.	Water. H^2O.	Valerianic aldehyde. $C^5H^{10}O$.	Butyl. C^8H^{18}.	Butyrate of ethyl. $C^6H^{12}O^2$.	Valerate of methyl. $C^6H^{12}O^2$.	Acetic acid. $C^2H^4O^2$.	Carbonate of ethyl. $C^5H^{10}O^3$.	Acetate of amyl. $C^7H^{14}O^2$.	° C.
0	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	0
10	10162	10152	10143	10132	10137	10138	10114	10130	10105	10119	10122	10130	10100	10001	10123	10121	10119	10114	10106	10118	10115	10
20	10337	10312	10292	10271	10277	10281	10233	10264	10213	10241	10247	10261	10202	10016	10251	10244	10242	10232	10213	10237	10231	20
30		10483	10450	10418	10421	10431	10355	10405	10324	10367	10378	10396	10305	10041	10385	10370	10368	10353	10321	10359	10348	30
40		10667	10620	10572	10573	10588	10482	10552	10440	10496	10514	10533	10411	10075	10523	10499	10498	10479	10432	10482	10467	40
50				10733	10735	10754	10612	10706	10562	10630	10655	10678	10519	10118	10667	10633	10634	10611	10545	10611	10589	50
60				10901	10912	10928	10749	10869	10691	10769	10804	10828	10631	10166	10816	10773	10775	10747	10662	10743	10715	60
70							10891	11040	10828	10914	10959	10984	10746	10223	10969	10919	10922	10888	10782	10880	10846	70
80								11221	10974	11064	11123	11151	10865	10286	11126	11071	11075	11036	10907	11021	10981	80
90										11220	11294	11325	10988	10354	11288	11233	11236	11190	11036	11169	11123	90
100											11475	11510	11115	10430	11452	11404	11405	11350	11172	11322	11271	100
110															11620	11585	11582	11518	11313	11483	11427	110
120																	11768	11692	11461	11651	11592	120
130																				11827	11766	130
140																					11949	140

TABLE B—*continued.*

° C.	Amylic alcohol. $C^5H^{12}O$.	Propionic acid. $C^3H^6O^2$.	Acetic anhydride. $C^4H^6O^3$.	Butyric acid. $C^4H^8O^2$.	Oxalate of methyl. $C^4H^6O^4$.	Cymene. $C^{10}H^{14}$.	Valerianic acid. $C^5H^{10}O^2$.	Bitter-almond oil. C^7H^6O.	Oxalate of ethyl. $C^6H^{10}O^4$.	Valerate of amyl. $C^{10}H^{20}O^2$.	Benzoate of methyl. $C^8H^8O^2$.	Phenol. C^6H^6O.	Benzoate of ethyl. $C^9H^{10}O^2$.	Benzylic alcohol. C^7H^8O.	Succinate of ethyl. $C^8H^{14}O^4$.	Naphthalene. $C^{10}H^8$.	Salicylate of methyl. $C^8H^8O^3$.	Cuminol. $C^{10}H^{12}O$.	Benzoic acid. $C^7H^6O^2$.	Cinnamate of ethyl. $C^{11}H^{12}O^2$.	Benzoate of amyl. $C^{12}H^{16}O^2$.	° C.
0	10000	10000	10000	10000	(The volume at the	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	(The volume at the	10000	10000	(The volume at the	10000	10000	0
10	10096	10110	10107	10105		10094	10105	10093	10108	10103	10090	10069	10093	10080	10101		10084	10084		10082	10084	10

20	10192	10222	10218	10212	melting-point, 50°, taken as unity.)	10190	10210	10186	10218	10207	10182	10142	10186	10160	10203	melting-point, 79·9°, taken as unity.)	10170	10169	melting-point, 121·4°, taken as unity.)	10165	10169	20
30	10289	10334	10333	10320		10286	10314	10277	10330	10318	10277	10218	10279	10242	10307		10257	10255		10249	10255	30
40	10388	10448	10451	10481		10385	10420	10368	10444	10420	10374	10298	10374	10325	10412		10345	10343		10335	10343	40
50	10490	10565	10574	10544	10000	10486	10528	10459	10561	10528	10472	10381	10469	10410	10518		10435	10431		10423	10438	50
60	10596	10683	10700	10660	10110	10589	10638	10551	10681	10639	10573	10466	10568	10496	10628		10526	10521		10513	10524	60
70	10708	10805	10830	10779	10222	10694	10749	10646	10805	10752	10677	10554	10666	10585	10740		10619	10612		10604	10617	70
80	10827	10930	10964	10901	10338	10801	10865	10741	10933	10869	10783	10647	10767	10677	10855	10006	10714	10705		10697	10713	80
90	10958	11059	11103	11027	10457	10914	10984	10839	11065	10992	10892	10742	10869	10771	10978	10083	10810	10800		10792	10810	90
100	11088	11192	11245	11157	10578	11028	11106	10939	11200	11117	11005	10841	10975	10866	11094	10163	10909	10898		10889	10910	100
110	11235	11329	11391	11291	10703	11146	11233	11042	11341	11247	11121	10943	11082	10964	11219	10247	11011	10999		10988	11012	110
120	11393	11472	11542	11430	10831	11268	11365	11149	11486	11383	11241	11048	11194	11066	11348	10335	11115	11102		11090	11117	120
130	11563	11620	11697	11574	10963	11394	11502	11260	11636	11524	11363	11157	11309	11170	11481	10426	11221	11209	10070	11194	11224	130
140	11748	11774	11856	11724	11097	11526	11646	11376	11791	11672	11489	11268	11428	11278	11619	10521	11330	11318	10153	11300	11383	140
150				11879	11235	11661	11795	11497	11952	11827	11621	11382	11551	11389	11762	10620	11441	11430	10240	11409	11445	150
160				12040	11376	11802	11953	11624	12119	11987	11755	11499	11678	11503	11911	10722	11557	11546	10329	11520	11560	160
170					11522	11948	12117	11757	12292	12156	11894	11618	11810	11620	12065	10827	11675	11666	10420	11635	11677	170
180						12099	12289	11896	12473	12332	12037	11741	11946	11742	12226	10937	11797	11790	10514	11751	11797	180
190									12659	12517	12184	11867	12088	11868	12392	11050	11923	11918	10610	11871	11919	190
200											12336	11996	12236	11998	12565	11166	12051	12051	10709	11993	12045	200
210													12389	12131	12744	11287	12185	12188	10810	12118	12173	210
220														12268	12931	11411	12322	12329	10913	12246	12305	220
230																	12462	12477	11020	12379	12439	230
240																		12630	11128	12514	12577	240
250																			11239	12652	12719	250
260																			11363	12794	12864	260
270																					13012	270

TABLE C.

° C.	Pierre.					Kopp.	Pierre.										Kopp.	Pierre.		° C.
	Bromide of methyl. CH^3Br.	Chloride of ethyl. C^2H^5Cl.	Bromide of ethyl. C^2H^5Br.	Sulphide of carbon. CS^2.	Iodide of methyl. CH^3I.	Chloride of acetyl. C^2H^3OCl.	Chloride of silicon. $SiCl^4$.	Iodide of ethyl. C^2H^5I.	Bromine. Br^2.	Chloride of monochlorethyl. $C^2H^4Cl^2$.	Chloroform. $CHCl^3$.	Chloride of dichlorethyl. $C^2H^3Cl^3$.	Trichloride of phosphorus. PCl^3.	Chloride of carbon. CCl^4.	Chloride of ethylene. $C^2H^4Cl^2$.	Sulphide of ethyl. $C^4H^{10}S$.	Chloral. C^2HCl^3O.	Chloride of amyl. $C^5H^{11}Cl$.	Disulphide of methyl. $C^2H^6S^2$.	
0	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	0
10	10146	10160	10135	10115	10122	10135	10132	10115	10106	10129	10115	10121	10114	10119	10113	10121	10094	10118	10103	10
20	10300	10327	10275	10235	10249	10276	10271	10232	10216	10260	10239	10249	10231	10241	10229	10247	10187	10237	10210	20
30			10423	10359	10382	10425	10419	10356	10327	10394	10369	10383	10351	10367	10348	10377	10281	10360	10320	30
40			10578	10490	10521	10580	10580	10484	10446	10532	10506	10524	10477	10497	10471	10513	10385	10485	10433	40
50				10628	10667	10742	10753	10614	10569	10675	10649	10670	10609	10631	10599	10653	10492	10615	10550	50
60						10910	10942	10749	10696	10825	10795	10822	10747	10772	10731	10809	10615	10750	10671	60
70								10885	10827	10984	10944	10979	10894	10916	10869	10953	10753	10891	10796	70
80												11143	11050	11074	11015	11113	10911	11039	10925	80
90															11166	11281	11091	11193	11057	90
100																11458	11298	11357	11194	100
110																		11532	11335	110
120																			11482	120

TABLE C—*continued.*

° C.	Kopp.	Pierre.			Kopp.	Pierre.					Kopp.		Pierre.				Kopp.			° C.
	Sulphydrate of amyl. $C^5H^{12}S$.	Bromide of amyl. $C^5H^{11}Br$.	Chloride of monochlorethylene. $C^2H^3Cl^3$.	Chloride of tin. $SnCl^4$.	Chloride of butylene. $C^4H^8Cl^2$.	Perchlorethylene. C^2Cl^4.	Bromide of ethylene. $C^2H^4Br^2$.	Chloride of dichlorethylene. $C^2H^2Cl^4$.	Chloride of arsenic. $AsCl^3$.	Chloride of titanium. $TiCl^4$.	Iodide of amyl. $C^5H^{11}I$.	Chloride of sulphur. S^2Cl^2.	Sulphite of ethyl. $C^4H^{10}SO^3$.	Chloride of trichlorethylene. C^2HCl^3.	Bromide of silicon. $SiBr^4$.	Bromide of phosphorus. PBr^3.	Chloride of benzoyl. C^7H^5OCl.	Chloride of antimony. $SbCl^3$.	Bromide of antimony. $SbBr^3$.	
0	10000	10000	10000	10000	10000	10000	(The volume at 20·00°,	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000	(The volume at the	(The volume at the	0
10	10105	10104	10106	10114	10096	10101		10090	10099	10096	10098	10096	10100	10092	10096	10085	10086			10

																		melting-point, 73·2°, taken as unity.)	melting-point, 90°, taken as unity.)	
20	10214	10212	10214	10231	10199	10208	taken as unity.)	10189	10200	10194	10198	10193	10208	10189	10194	10171	10174			20
30	10326	10325	10324	10350	10306	10308	10096	10295	10303	10295	10302	10290	10308	10288	10298	10259	10262			30
40	10442	10441	10437	10473	10419	10416	10195	10404	10408	10399	10408	10388	10416	10391	10398	10347	10353			40
50	10561	10562	10554	10599	10538	10529	10297	10516	10516	10506	10517	10488	10526	10494	10496	10438	10444			50
60	10685	10687	10677	10729	10660	10648	10402	10622	10626	10616	10628	10590	10639	10600	10599	10529	10537			60
70	10813	10816	10805	10864	10788	10778	10510	10734	10739	10729	10744	10694	10754	10706	10705	10623	10632			70
80	10944	10950	10935	11003	10920	10903	10620	10849	10854	10844	10864	10802	10872	10813	10812	10719	10729	10055		80
90	11080	11089	11069	11149	11054	11031	10734	10968	10972	10964	10987	10913	10994	10925	10921	10816	10829	10138	10000	90
100	11220	11238	11208	11300	11194	11160	10850	11090	11094	11086	11112	11028	11118	11040	11031	10916	10930	10223	10059	100
110	11365	11388	11349	11457	11336	11290	10970	11217	11218	11211	11243	11147	11245	11159	11143	11018	11035	10310	10120	110
120	11514	11539	11496	11620	11482	11421	11098	11348	11345	11340	11377	11271	11376	11282	11258	11122	11142	10400	10185	120
130					11631	11552	11223	11483	11475	11472	11516	11402	11510	11410	11373	11227	11252	10491	10252	130
140							11360	11621	11610	11607	11658	11537	11647	11542	11490	11335	11364	10584	10322	140
150											11806	11677	11787	11681	11609	11444	11479	10680	10394	150
160													11930	11826	11730	11555	11598	10777	10469	160
170																11668	11721	10877	10547	170
180																11783	11847	10978	10627	180
190																	11978	11082	10711	190
200																	12112	11187	10797	200
210																		11295	10885	210
220																		11405	10977	220
230																		11517	11071	230
240																			11167	240
250																			11267	250
260																			11369	260
270																			11478	270
280																			11580	280

Expansion of Liquids under Pressure.

Observer .	DRION.*			ANDRÉEFF.					MENDELEJEFF.				REGNAULT.	
Name of substance . . .	Chloride of ethyl.	Peroxide of nitrogen	Sulphurous anhydride.		Sulphurous anhydride.	Ammonia.	Nitrous oxide.	Carbonic anhydride.	Ether.		Alcohol.		Air.	
Boiling-point	+ 11°	+ 28°	− 8°		−10°	− 34°.	− 87·9°.	− 78·2°.	+34 9°.		+78·4°.			
0° C.	100000	100000	100000	−10° C.	9808	9805		9517	0° C.	10000	0° C.	10000	−10°C.	9634
10	101535	101480	101806	−5	9903	9900	9786	9754	78·2°	11508			0	10000
20	103176	103029	103756	0	10000	10000	10000	10000	99·8	12091	99·9°	11294	+10	10366
30	104933	104673	105865	+5	10099	10105	10211	10270	131·2	13150	130·9	11895	20	10733
									157·0	14235			30	11099
40	106798	106442	108140	10	10200	10215	10453	10585					40	11466
50	108771	108367	110607	15	10303	10330	10766	10969					50	11832
60	110889	110484	113311	20	10408	10450	11202	11457					60	12199
70	113176	112828	116300	25	10516			12095					70	12565
													80	12932
80	115670	115440	119664	30	10625								90	13298
90	118426	118365	123516	35	10738								100	13665
100	121490		127958	40	10853									
110	124927		133285										110	14031
													120	14398
120	128871		139797										130	14764
130	133540		148365										140	15131
													150	15497
													160	15864

* The volumes given by Drion are the *apparent* volumes, uncorrected for the expansion of the glass : the corrected, or true, volumes would be a little greater.

gases, or even more rapidly, for equal increments of temperature. Determinations of the expansion of water above 100°, by Mendelejeff, have already been given (p. 59); the preceding table (p. 66) contains the results of the observations of Drion (Ann. Ch. Phys. [3] lvi. 5), Andréeff (*ibid.* lvi. 317), and Mendelejeff (*loc. cit.*) on some other liquids at temperatures above their usual boiling points. To serve as a standard of comparison, the expansion of air is given in the last column of the table.

Expansion of Solids.—In speaking of the expansion of solid bodies, it is needful to distinguish between *linear* expansion, or the increase in length of a linear unit; *superficial* expansion, or the increase in the area of a unit of surface; and *cubical* expansion, or the increase in bulk of a unit of volume. If a solid body, whose length is A linear units, expands, when heated from 0° C. to 1°, so as to measure $A + a$ at the higher temperature, a portion of its surface containing A^2 superficial units at the lower temperature will become $(A + a)^2$ when expanded, and, at the same time, the volume A^3 will become $(A + a)^3$. We have therefore for the increase in length, or

$$\begin{array}{lll} \text{linear expansion,} & A + a - A & = a; \text{ for the} \\ \text{superficial expansion,} & (A + a)^2 - A^2 & = 2Aa + a^2; \text{ for the} \\ \text{cubical expansion,} & (A + a)^3 - A^3 & = 3A^2a + 3Aa^2 + a^3. \end{array}$$

But since a is always a very small fraction of A, a^2 is also a very small fraction of a; hence the second and third terms of these expressions may be omitted. Accordingly, the expansion of A linear units may be taken as a, the expansion of A^2 superficial units as $2Aa$, and the expansion of A^3 cubical units as $3A^2a$. The *coefficients* of linear, superficial, and cubical expansion, or the expansion of one unit of each kind, will therefore be respectively

$$\frac{a}{A}, \quad \frac{2Aa}{A^2} = 2\,\frac{a}{A}, \quad \text{and} \quad \frac{3A^2a}{A^3} = 3\,\frac{a}{A};$$

that is to say, the coefficient of superficial expansion is *twice* as great, and the coefficient of cubical expansion *three times* as great as the coefficient of linear expansion.

When a hollow vessel is heated, its capacity increases to exactly the same extent as it would do if filled with the substance of which its sides are composed; that is, its expansion is the same as the cubical expansion of a solid mass of the same material and dimensions. If κ be the coefficient of cubical expansion of any kind of glass for a rise of temperature of 1° C., a vessel made of this glass and having the capacity V_0 at 0°, would have at t° the capacity $V_1 = V_0\,(1 + \kappa\,t)$. Similar considerations are applicable in the case of a glass vessel which is divided into parts of equal capacity by a scale etched upon the side, when the space comprised between two consecutive divisions at 0° is taken as the unit of capacity. The apparent volume V_1, read off at t°, would then correspond to the real volume $V_0\,(1 + \kappa\,t)$ referred to the unit adopted.

Determinations of Linear Expansion.—The linear expansion has been measured for the greater number of such substances as can be obtained in the form of rods or bars of considerable length. For the purpose of such measurements, one end of the bar is fixed immovably, and its length is measured, by means of micrometric apparatus attached to the other end, at two known temperatures, such as 0° and 100° C., which can be maintained constant sufficiently long to make it certain that they have been attained by the bar throughout its whole mass. The following table of linear expansions between 0° and 100° C. is from Ure's *Dictionary of Chemistry*, ed. 1836, pp. 271, 272.

Linear Expansion of Solids by Heat.

		Dimensions which a bar takes at 100° C. whose length at 0° is 1·000000.	Expansion.
Glass tube	Smeaton	1·00083333	
„	Roy	1·00077615	
„	Deluc's mean	1·00082800	$\frac{1}{1116}$
„	Dulong and Petit	1·00086180	$\frac{1}{1148}$
„	Lavoisier and Laplace	1·00081166	$\frac{1}{1122}$
Plate glass	„ „	1·000890890	$\frac{1}{1142}$
„ crown glass	„ „	1·00087572	$\frac{1}{1114}$
„ „	„ „	1·00089760	$\frac{1}{1090}$
„ „	„ „	1·00091751	
„ rod	Roy	1·00080787	
Deal	Roy	as glass	
Platinum	Borda	1·00085655	$\frac{1}{1167}$
„	Dulong and Petit	1·00088420	$\frac{1}{1131}$
„	Troughton	1·00099180	
„ and glass	Berthoud	1·00110000	

Linear Expansion of Solids by Heat.

Dimensions which a bar takes at 100° C. whose length at 0° is 1·000000.

			Expansion.
Palladium	Wollaston	1·00100000	
Antimony	Smeaton	1·00108300	
Cast-iron prism	Roy	1·00110940	
Cast-iron	Lavoisier, by Dr. Young	1·00111111	
Steel	Troughton	1·00118990	
Steel rod	Roy	1·00114470	
Blistered steel	Phil. Trans. 1795, 428	1·00112500	
„ „	Smeaton	1·00115000	
Steel not tempered	Lavoisier and Laplace	1·00107875	$\frac{1}{927}$
„ „	„ „	1·00107956	$\frac{1}{926}$
„ tempered yellow	„ „	1·00136900	
„ „ „	„ „	1·00138600	
„ „ „ at a higher heat	„ „	1·00123956	$\frac{1}{807}$
Steel	Troughton	1·00118980	
Hard steel	Smeaton	1·00122500	
Annealed steel	Muschenbroek	1·00122000	
Tempered steel	„	1·00137000	
Iron	Borda	1·00115600	
„	Smeaton	1·00125800	
Soft iron, forged	Lavoisier and Laplace	1·00122045	
Round iron, wire drawn	„ „	1·00123504	
Iron wire	Troughton	1·00144010	
Iron	Dulong and Petit	1·00118203	$\frac{1}{846}$
Bismuth	Smeaton	1·00139200	
Annealed gold	Muschenbroek	1·00146000	
Gold	Ellicot, by comparison	1·00150000	
„ procured by parting	Lavoisier and Laplace	1·00146606	$\frac{1}{682}$
„ Paris standard, unannealed	„ „	1·00155155	$\frac{1}{645}$
„ „ „ annealed	„ „	1·00151361	$\frac{1}{661}$
Copper	Muschenbroek	1·00191000	
„	Lavoisier and Laplace	1·00172244	$\frac{1}{581}$
„	„ „	1·00171222	$\frac{1}{584}$
„	Troughton	1·00191880	
„	Dulong and Petit	1·00171821	$\frac{1}{582}$
Brass	Borda	1·00178300	
„	Lavoisier and Laplace	1·00186671	
„	„ „	1·00188971	
Brass scale, supposed from Hamburg	Roy	1·00185540	
Cast Brass	Smeaton	1·00187500	
English plate-brass, in rod	Roy	1·00189280	
„ „ in a trough form	„	1·00189490	
Brass	Troughton	1·00191880	
„ wire	Smeaton	1·00193000	
„	Muschenbroek	1·00216000	
Copper 8, tin 1	Smeaton	1·00181700	
Silver	Herbert	1·00189000	
„	Ellicot, by comparison	1·00210000	
„	Muschenbroek	1·00212000	
„ of cupel	Lavoisier and Laplace	1·00190974	$\frac{1}{524}$
„ Paris standard	„ „	1·00190868	$\frac{1}{524}$
Silver	Troughton	1·00208260	
Brass 16, tin 1	Smeaton	1·00190800	
Speculum metal	„	1·00193300	
Spelter solder; brass 2, zinc 1	„	1·00205800	
Malacca tin	Lavoisier and Laplace	1·00193765	$\frac{1}{516}$
Tin from Falmouth	„ „	1·00217298	$\frac{1}{462}$
Fine pewter	Smeaton	1·00228300	
Grain tin	„	1·00248300	
Tin	Muschenbroek	1·00284000	
Soft solder; lead 2, tin 1	Smeaton	1·00250800	
Zinc 8, tin 1, a little hammered	Smeaton	1·00269200	
Lead	Lavoisier and Laplace	1·00284836	$\frac{1}{351}$
„	Smeaton	1·00286700	
Zinc	„	1·00294200	

Linear Expansion of Solids by Heat.

		Dimensions which a bar takes at 100° C. whose length at 0° is 1·00000.	Expansion.
Zinc, hammered out ½ inch per foot	Smeaton	1·00301100	
Glass, from 0° to 100°	Dulong and Petit	1·00086130	$\frac{1}{1161}$
„ from 100° to 200°	„ „	1·00091827	$\frac{1}{1089}$
„ from 200° to 300°	„ „	1·000101114	$\frac{1}{987}$

The last two measurements by an air-thermometer.

Messrs. Calvert, Johnson, and Lowe have determined the linear expansion of a considerable number of metals and alloys by a modification of the method above described, for the details of which we must refer to the original paper published in the *Mechanics' Magazine*.

The following are the linear expansions of simple metals between 0° and 100° C. thus determined:—

Cadmium (pure)	0·00332
Lead (pure)	0·00301
Tin (pure)	0·00273
Aluminium (commercial)	0·00222
Zinc, forged (pure)	0·00220
Silver (pure)	0·00199
Gold (pure)	0·00138
Bismuth (pure)	0·00133
Wrought iron	0·00119
Cast iron	0·00112
Steel (soft)	0·00103
Antimony (pure)	0·00098
Platinum (commercial)	0 00068

From the preceding table it will be seen that the coefficients of expansion of the metals vary with their physical condition, being different for the same metal according as it has been cast, hammered and rolled, hardened, or annealed. As a general rule, those operations which increase the density, appear also to increase the rate of expansion by heat. But even for substances in apparently the same condition, different observers have found very unequal amounts of expansion; this may arise, in the case of compound substances, such as glass, brass, or steel, from a want of uniformity in chemical composition, and in simple bodies from slight differences of physical state. Hence, in all cases where great accuracy is required in the determination of the linear expansion, as in rods employed for pendulum observations, or for the measurement of the base-lines of surveys, it is impossible to rely upon the results of previous determinations of the expansion of the material in question; but the linear expansion of each individual rod must be determined by a special experiment: this was done, for instance, by De Borda, with each of the four platinum measuring rods (each two toises, or twelve French feet long), which were employed in the measurement of the arc of meridian, from which the length of the metre was deduced.

Copper rods were laid upon the platinum rods, and both were firmly fixed together at one end; the copper rods carried a divided scale at the other end, which indicated directly the twenty-thousandth part of their length, while by means of a vernier attached to the corresponding end of the platinum rods, tenths of these divisions, or about the one-hundredth part of a French line, could be read off. In this way, the difference in the expansion of two rods of the same length but different materials can be determined with great accuracy, and if the coefficient of expansion for the material of one rod is known, the coefficient of that of the other can be calculated.

If both rods have the same length, L, at 0°, and at $t°$ one has the length $L' = L(1 + \alpha t)$, the other the length $L'' = L(1 + \alpha' t)$, we have $L' - L'' = L t (\alpha - \alpha')$. But $L' - L''$ is the observed difference of length at the temperature $t°$; and hence if α is known, α' is easily calculated. In this way, Dulong and Petit deduced the linear expansion of copper from that of platinum.

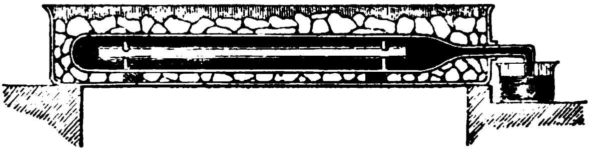
If, on the other hand, the expansion of the material of two rods thus united is known, and can be taken as proportional, within certain limits of temperature, to the indications of the mercurial thermometer, the combination of the two rods may be employed as a metallic thermometer. The measurement of temperatures in this way is specially valuable in the case of standard measures of length, which can thus be made to indicate their own temperature. If, for instance, the two rods have the same length at 0°, and differ at 100° by the amount D, and at $t°$ by the amount d, the temperature is given by the equation $t = \frac{d}{D} 100$.

The unequal expansion of different metals has been taken advantage of for the construction of thermometers of another kind. If two straight strips of different metals are fastened together throughout their whole length, any variation of temperature must cause the compound strip to bend, so that the least expanded metal will be on the concave side, and the most expanded metal on the convex side of the curve. **Breguet's** thermometer, constructed upon this principle, is made from a compound plate of platinum, gold, and silver, soldered together, the gold in the middle. This is rolled out very thin, and cut into very narrow strips, which are coiled round into spirals. The thermometer consists of such a spiral suspended by one end from a support, and carrying a needle which swings round a divided circle at the other.

Supposing the silver to be inside of the spiral, any rise of temperature will be indicated by the untwisting of the spiral, and a fall of temperature by its twisting more tightly. The small mass of this instrument, and the low specific heat of the materials composing it, cause it to indicate changes of temperature very rapidly, and to be affected by very small quantities of heat.

Determinations of Cubical Expansion.—When the coefficient of linear expansion of a substance is known, its coefficient of cubical expansion is obtained by multiplying the linear coefficient by 3, as already explained (p. 67). The cubical expansion can also be ascertained by direct measurement. The following method was employed by Dulong and Petit for this purpose: Into a glass tube, 18 millimetres wide, 6 decimetres long, and closed at one end, they introduced a rod, previously weighed, of a metal not attacked by mercury. Let W' be its weight. The tube was then drawn out at the open end and bent as in *fig.* 536, after which it was filled with pure mercury, and boiled out to remove every trace of air, exactly as in filling a mercurial thermometer. In this state the apparatus was placed horizontally, and surrounded with melting ice, the point dipping below the surface of mercury contained in a small capsule. It was thus filled with mercury at 0°. The capsule was next emptied, replaced under the point, and the apparatus allowed again to assume the temperature of the atmosphere. Then, by weighing together the tube and capsule, and deducting from the gross weight their weight before the introduction of the mercury, they obtained the weight, W, of the mercury which exactly filled at 0° so much of the capacity of the tube as was not occupied by the metal rod. The experiment was completed by heating the instrument in an oil-bath to a high temperature, T, and weighing the quantity of mercury which escaped from the point, as in the determination of a temperature by means of the weight-thermometer (p. 18).

Fig. 536.



If D_0 and D_0' represent the densities at 0° of mercury and of the metal; Δ, x, and κ, the coefficients of cubical expansion of mercury, of the metal, and of glass respectively, their volumes at 0° will be represented by

$$\frac{W}{D_0}, \quad \frac{W'}{D_0'}, \quad \text{and} \quad \left(\frac{W}{D_0} + \frac{W'}{D_0'}\right);$$

and if w is the weight of mercury which escapes from the tube between 0° and t°, the weight of mercury remaining in the tube at the latter temperature will be $W - w$. Then putting the volume of this weight of mercury at the temperature t, together with that of the metal rod at the same temperature, equal to the capacity of the tube which contains them, we have

$$\frac{W-w}{D_0}(1 + \Delta t) + \frac{W'}{D_0'}(1 + x t) = \left(\frac{W}{D_0} + \frac{W'}{D_0'}\right)(1 + \kappa t);$$

whence

$$x = \frac{w D_0'}{W' D_0} + \frac{D_0'}{W'}\left\{\left(\frac{W}{D_0} + \frac{W'}{D_0}\right)\kappa - \left(\frac{W-w}{D_0}\right)\Delta\right\}$$

It is of course necessary that the values of Δ and κ should have been determined by previous experiments in the way already described.

Another, to some extent similar, method of measuring the cubical expansion of solid bodies, consists in determining their specific gravities at various temperatures, the bulk of a given weight of a substance being inversely as its density.

In applying this method, the weight of water free from air which fills a specific-gravity bottle at various temperatures is first ascertained; then, the weight of the bottle is determined at the same temperatures after a known weight of the substance under examination has been put into it, and the interstices filled with water. Let W be the weight of water which fills the bottle at the temperature t, W' the weight of the solid substance, and S the weight of water and solid substance which together fill the bottle at $t°$; then the density of the substance at $t°$, compared with that of water at the same temperature, is $D_t = \frac{W'}{W-(S-W')}$; and if V_t represents the bulk which a unit-volume of water measured at 0° assumes at $t°$, the density of the substance at $t°$, compared with that of water at 0°, is $\frac{D_t}{V_t} = D_0$. Lastly, if the density D_0' of the substance at some other temperature $t'°$, has been determined in the same way, its mean coefficient of cubical expansion for one degree between $t°$ and $t'°$ is $\frac{D_0 - D_0'}{(t'-t)D_0'}$.

Table of Coefficients of Cubical Expansion of Solids for 1° C.

Substance.	Coefficient.	Interval of Temperature.	Observer.
Glass	$\frac{1}{38700}$ = 0·0000258	0° to 100°	Dulong
„	$\frac{1}{36300}$ = ·0000275	0 „ 200	„
„	$\frac{1}{32900}$ = ·0000304	0 „ 300	„
Soft French glass . .	·0000260	17 „ 99	Kopp
„ „ another kind	·0000253	7 „ 99	„
Hard potash glass . .	·0000209	16 „ 100	„
Common glass . . .	$\frac{1}{36230}$ = ·0000276	0 „ 100	Regnault
„ „	$\frac{1}{32720}$ = ·0000306	0 „ 300	„
Crystal glass from Choisy-le-Roi . . .	$\frac{1}{43860}$ = ·0000228	0 „ 100	„
„ „ „	$\frac{1}{42918}$ = ·0000233	0 „ 300	„
Iron	$\frac{1}{28200}$ = ·0000355	0 „ 100	Dulong
„	$\frac{1}{22700}$ = ·0000441	0 „ 300	„
„ (soft wire). . .	·0000370	13 „ 100	Kopp
Copper	$\frac{1}{19400}$ = ·0000515	0 „ 100	Dulong
„	$\frac{1}{17700}$ = ·0000565	0 „ 300	„
„ (wire) . . .	·0000518	11 „ 99	Kopp
Platinum	$\frac{1}{37700}$ = ·0000265	0 „ 100	Dulong
„	$\frac{1}{36300}$ = ·0000275	0 „ 300	„
Lead	·0000889	11 „ 100	Kopp
Tin	·0000689	12 „ 99	„
Zinc	·0000898	11 „ 44	„
Cadmium	·0000936	12 „ 43	„
Bismuth	·0000400	12 „ 41	„
Antimony	·0000331	12 „ 43	„
Sulphur	·0001826	14 „ 46	„
Lead-glance	·0000680	14 „ 48	„
Zinc-blende	·0000358	15 „ 45	„
Iron-pyrites	·0000338	15 „ 47	„
Rutile	·0000322	14 „ 46	„
Tin-stone (SnO^2) . .	·0000163	16 „ 46	„
Specular iron . . .	·0000404	13 „ 47	„
Magnetic iron ore . .	·0000291	17 „ 50	„
Fluor-spar	·0000623	14 „ 47	„
Arragonite	·0000647	10 „ 43	„
Calc-spar.	·0000175	9 „ 42	„
Bitter-spar	·0000352	13 „ 43	„
Spathic iron-ore . .	·0000350	14 „ 45	„
Heavy spar	·0000581	12 „ 42	„
Cœlestine	·0000608	12 „ 45	„
Orthoclase	·0000225	13 „ 99	„
Quartz	·0000403	18 „ 100	„
Bayeux porcelain . .	·0000108	0 „ 860	Deville and Troost
„ „ . .	·0000108	0 „ 1000	„

The cubical expansion of a considerable number of crystallised compounds has also been determined by Joule and Playfair (Chem. Soc. Qu. J. i. 121; for a table of the results, see also Gmelin's *Handbook*, i. 234).

From the determinations given at the beginning of this table, it will be seen that the coefficients of expansion of solid bodies become greater as the temperature rises; but that the coefficient of expansion of platinum, which at the temperatures of the experiments is very far from the point at which fusion or softening occurs, increases much less than the coefficients of expansion of the more fusible metals, copper and iron. The rule thus indicated has been found to be verified in other cases also, so that with solids, as well as with liquids, the coefficients of expansion remain sensibly constant at temperatures far removed from those at which change of state occurs, and vary more and more rapidly as these latter temperatures are approached.

The expansion of amorphous solids, and of those which crystallise in the regular system (CRYSTALLOGRAPHY, ii. 121), is the same for all dimensions, unless when they are subject to a mechanical strain in some particular direction. A fragment of such a substance varies in bulk with variations of temperature, but retains always the same shape.

Crystals not belonging to the regular system exhibit when heated an unequal expansion in the direction of their axes, in consequence of which the magnitude of their angles becomes altered (Mitscherlich, Pogg. Ann. i. 125; x. 137). In crystals belonging to the trimetric system, the expansion is different in the direction of all three axes; in arragonite, on raising the temperature from 0° to 100°, the inclination of the lateral faces increases by 2′ 46″, and that of the terminal faces diminishes by 5′ 29″; gypsum is, according to Fresnel (Bull. des Sc. Mathem. 1824, 100; also Pogg. Ann. ii. 109), more expanded by heat in the direction of the principal axis than in that of the lateral axes. In crystals belonging to the hexagonal system, the expansion is the same in the directions of the three secondary axes; but different from that according to the principal axis. The obtuse angles of the primitive rhombohedron of calcspar diminish by 8½′ when the crystal is heated 100°, and the acute angles increase by the same quantity. Hence it may be calculated that the relative expansion of the principal axis (compared with that of the secondary axes) amounts to 0·00342; moreover since, according to Mitscherlich and Dulong, the cubical expansion of calcspar between 0° and 100° is only 0·001961, it may likewise be determined that calcspar, when thus heated, does not expand in the direction of the secondary axes, but *contracts* by 0·00056, and that the absolute expansion of the principal axis may be estimated at 0·00286. In bitter-spar, the obtuse angle of the primitive rhombohedron diminishes when the temperature is raised from 0° to 100° by 4′ 6″, in ferruginous bitter-spar by 3′ 29″; in iron-spar containing a considerable quantity of manganese, by 3′ 31″, and in pure iron-spar by 2′ 22″. Since now, among all these minerals, calcspar forms the least, and ferruginous bitter-spar the most obtuse rhombohedron, it follows that the expansion in the direction of the principal axis does not increase in the same proportion as the relative length of the axis itself diminishes (Mitscherlich).

The following direct determinations of the linear expansion of several crystallised substances, between 0° and 100°, made by Pfaff (Jahresber. 1858, 7), show very distinctly the inequality in the amounts of expansion in the direction of the different axes.

Linear Expansion of Crystals between 0° *and* 100°

Monometric Crystals.		Dimetric or Hexagonal Crystals.		
Substance.	Expansion.	Substance.	Expansion.	
			Principal Axis.	Secondary Axes.
Garnet	0·0008478	Tin-stone	0·0004860	0·0004526
Iron-pyrites	·0010084	Vesuvian	·0007872	·0009629
Magnetic iron	·0009540	Zircon	·0006264	·0011054
Lead-glance	·0018594	Beryl	·0001721	−0·0000132
Fluor-spar	·0019504	Corundum	·0006876	·0006551
		Quartz	·0008073	·0015147
		Tourmaline	·0009369	·0007732
		Calc-spar	·0026261	−0·0003105

NOTE.—A minus sign (−) in the last column denotes contraction, instead of expansion.

This alteration of shape caused by change of temperature is most easily rendered evident in gypsum, of which substance twin-crystals often occur, having pretty nearly the form shown in *fig.* 537. From such a crystal, a portion *a b*, *c d* is cut, so that the new surfaces are perpendicular to the surface of combination, *m n*, of the two halves of the crystal, and the face *a b* is ground and polished. At the temperature of the atmosphere, this surface then constitutes a single, unbroken plane; but when it is heated to about 60° or 80° C., the shape of the crystal alters in the manner shown in *fig.* 538, and now parallel rays of light falling on the two halves from a distant object are reflected in different directions, so that two distinct images of the object may be seen simultaneously by reflection from the surface *a b*.

Fig. 537.

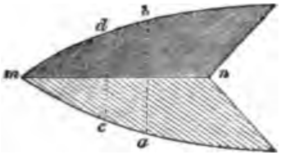
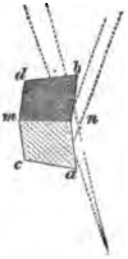


Fig. 538.



One or two solid bodies are known which, at least within certain limits of temperature, form exceptions to the general rule of expansion by heat, and contract as their temperature is raised. For example, the alloy of 2 pts. bismuth, 1 pt. tin, and 1 pt. lead, expands when heated from 0° to 44° C.; when still further heated, it contracts, so that at 56° its density is the same as it was at 0°, and at 69° still greater; beyond this temperature, expansion again takes place; at 87·5° the alloy has once more the same density as at 0°, and at 94°, at which it fuses, the same as at 44°. (Erman, Pogg. Ann. ix. 557. For the not quite concordant results of H. Kopp, see below, p. 78.)

Again, a piece of vulcanised caoutchouc, which is stretched by a weight to double its length, is shortened by a tenth when its temperature is raised 50° C., and the shortening effect increases rapidly with the stretching weight employed. (Joule, Proc. Roy. Soc. viii. 356.)

Relation between the Specific Heats of Liquid and Solid Bodies, and their Coefficients of Expansion at different temperatures.—It has been pointed out above (p. 40), that the specific heat of any substance includes, not only the portion of heat required to cause in it a given alteration of temperature, but also the quantity of heat which is expended in modifying its condition of molecular equilibrium, and whose most obvious external effect is an alteration of the volume of the substance. We have also seen (p. 44), that although no certain data exist for calculating the ratio of these two parts of the total specific heat, except in the case of gases, it is nevertheless probable that the former part, or the *real specific heat* of a substance, remains the same for all conditions. Hence variations in the total or *apparent specific heat* must be supposed to result from variations in the amount of heat expended in overcoming the molecular forces. In sensibly perfect gases, the consumption of heat in this manner is the same at all temperatures, and so small as to be negligible; accordingly, both the real and apparent specific heats of gases are constant at all temperatures (pp. 34 and 42). On the other hand, the molecular changes which accompany alterations of temperature in liquid and solid bodies are such as require the expenditure of very considerable quantities of heat to produce them. These changes doubtless consist in alterations of the relative position or arrangement of the molecules, but of what precise kind we have no means of ascertaining, since the only measurable portion of the total effect is the externally visible change of volume.

This change of volume cannot be taken as in every case a measure of the amount of molecular work performed by the heat independently of causing alteration of temperature; for, as we have seen (p. 59), the communication of heat to water below 4° C. causes a change of bulk of the opposite kind to that which it occasions above that temperature; but we may nevertheless probably admit without great error that, as a general rule, the proportion of the total quantity of heat required to raise the temperature of a given substance 1°, which is consumed in producing molecular changes, is greatest at those points of the thermometric scale at which the greatest amount of expansion accompanies a rise of temperature of 1°, and is least at those points at which the corresponding expansion is least. If this supposition be admitted, it accounts satisfactorily for the fact that both the specific heats of solid and liquid bodies and their coefficients of expansion increase, as a rule, with rise of temperature; and that both these properties vary most rapidly in the neighbourhood of those temperatures at which changes of the state of aggregation occur (Comp. Verdet, *Exposé de la Théorie Mécanique de la Chaleur,* Paris, 1863, note G, pp. 133 *et seq.*; also Regnault, Mem. Acad. Sciences, xxvi. 285 *et seq.*) On the relations between changes of volume produced by external forces and the corresponding evolution or disappearance of heat, see below: Relations of Heat to Mechanical Energy.

3. *Changes of State of Aggregation produced by Heat.*

Fusion and Solidification.—When the temperature of a solid body is raised continuously, a point is reached sooner or later at which it melts, or exchanges the solid for the liquid form; and when a liquid is cooled, a point is in like manner attained at which it solidifies. With most homogeneous substances, the passage from the one state to the other takes place suddenly at some particular temperature; thus ice, when heated from a lower temperature to 0° C., becomes only very slightly softer or less solid, while if more heat still is imparted to it, it changes at once into perfectly liquid water. This temperature forms a definite limit below which we have solid ice, and above which we have liquid water, and it is therefore called the *melting point* of ice. Some substances, however, pass when heated from the solid to the liquid state without showing any definite melting point; for example, glass and iron become gradually softer and softer when heated, and pass by imperceptible stages from the solid to the liquid condition. Such substances may be said to begin to melt at the lowest temperature at which perceptible softening occurs, and to be fully melted when further elevation of temperature does not make them sensibly more fluid; but no precise temperatures can be given as their melting points.

Subject to the qualifications hereafter stated, the following general laws may be taken as applicable to the phenomena of fusion and solidification:—

1°. The state of aggregation of every substance is always the same at the same temperature: when its temperature is raised, it melts at a certain fixed point, or passes from the solid to the liquid state, and when its temperature is lowered, it solidifies, or passes from the liquid to the solid state, at a point which is also fixed, and is the same as its melting-point. (For substances which melt gradually, a certain fixed interval must be substituted for a fixed point of temperature in the enunciation of this rule.)

2°. The communication of heat to a solid body at its melting point causes it to melt, but does not raise its temperature; so also the withdrawal of heat from a liquid at its freezing point causes it to solidify, but does not lower its temperature.

3°. As a general rule, a sudden change of volume (usually an increase) accompanies the passage from the solid to the liquid state.

We will proceed to consider each of these laws and the exceptions and modifications to which they are subject.

Melting and Freezing Points.—Though the temperature at which the passage from the solid to the liquid state takes place, and *vice versâ,* is constant (under the same circumstances) for each substance, the melting and freezing points of different substances vary within very wide limits. Thus sulphurous anhydride melts at − 80° (Mitchell, *Berzel. Jahresber.* xxii. 59), mercury at − 40°, bromine at − 7·3°, ice at 0°, phosphorus at + 44°, tin at 235°, silver at 1000°, platinum at 2000° (Deville and Debray). (For the melting points of particular substances, see the articles in this Dictionary where they are respectively described.)

These differences are sufficient to justify the conclusion that even those substances which have never been seen to melt, would do so at a sufficiently high temperature, and conversely that all liquids, even such as have never yet been frozen, would solidify if exposed to a still more intense degree of cold. Indeed, in proportion as new methods of producing extreme temperatures have been discovered, the number of infusible solids and non-solidifiable liquids has gone on diminishing continually. The only substances which can be considered really infusible are those which, when heated, undergo chemical alteration before their melting point is reached. The most infusible of all substances which are chemically inalterable by heat is, probably, carbon in the form of graphite, and even this body was found by Despretz to soften when exposed to the heat produced by the electric current generated by 600 Bunsen's cells arranged in six series of 100. On the other hand, absolute alcohol, sulphide of carbon, and some other liquids have never been solidified, but at the temperature produced by a mixture of liquid nitrous oxide, solid carbonic anhydride, and ether, Despretz found that absolute alcohol became so viscid that it did not run out on inverting the vessel that contained it.

In very many cases, it happens that a mixture of two or more substances melts at a lower temperature than either of its components taken separately: thus, a mixture of 1 part chloride of sodium with 2½ or 2¾ parts ice, melts at about −20°; mixtures of fatty acids melt at lower temperatures than the pure acids; the carbonates of potassium and sodium melt more easily when mixed than either salt does alone; Rose's fusible alloy of 2 parts bismuth, 1 part tin, and 1 part lead, melts between 95° and 98°; an alloy of 1 or 2 parts cadmium with 2 parts tin, 4 parts lead, and 7 or 8 parts bismuth, melts between 66° and 71° (B. Wood); &c.

In homologous series of analogous organic compounds, the melting point of each term usually rises with its atomic weight.

Under particular circumstances liquids may be cooled below the melting point of the corresponding solid body, without solidifying. This occurs especially when they are cooled very slowly, and are at the same time protected from all mechanical disturbance. For instance water at perfect rest, and under a pressure somewhat greater than that of the atmosphere, may be cooled to −15° without freezing, but contact with a solid body or the slightest agitation is then usually sufficient to cause solidification to commence. The smaller the quantity of liquid operated upon, the lower is the temperature to which it can be cooled, and the greater the mechanical disturbance which it will support without freezing. Thus, **Fournet** (Ann. Ch. Phys. [3] xlvi. 203) has remarked the frequent occurrence of mists formed by particles of liquid water suspended in an atmosphere of which the temperature was 10, 12, or even 15 degrees below zero; and Sorby found that in glass tubes of 0·1 millimetre in diameter, water could be maintained in the liquid state as low as −17°.

Some remarkable phenomena of this kind have been also observed by **Dufour** (Ann. Ch. Phys. [3] lxviii. 370) in the case of liquids cooled without contact with any solid body. His method of experimenting was to suspend globules of the liquid under examination in some other liquid of the same specific gravity, but of lower freezing point, and in which it was insoluble. Water was examined while suspended in a mixture of chloroform and sweet oil of almonds; sulphur and phosphorus, in an aqueous solution of chloride of zinc; and naphthalene, in water. In the experiments with water, the spheres of this liquid which floated in the mixture of chloroform and oil were very rarely seen to freeze at 0°; in general, solidification occurred between −4° and −12°, the smallest globules, as a rule, remaining liquid to a lower temperature than the larger ones, some of them having been repeatedly seen still liquid at −18° or −20°. Agitation and the contact of solid bodies appears to have much less effect in causing the solidification of liquids cooled in this way than when they are cooled to the same extent in glass vessels. For instance, Dufour found that the globules of water in his experiments often did not solidify when displaced or violently deformed by a glass rod, and even that crystals of chloride of sodium, sulphate or nitrate of potassium, sugar, &c., would sometimes fall *through* a globule of water 5 millimetres in diameter, and cooled to at least −8°, without producing any effect. Contact with a fragment of ice, however, invariably caused immediate congelation.

By operating as above described, Dufour obtained globules of sulphur (melting point 115°) of 6 millimetres diameter still liquid at 40°, and globules of 0·5 millimetre diameter remained liquid for several days at 5° or 10°. Globules of phosphorus of considerable size were cooled to 20°, and globules of 1 or 2 millimetres diameter to 0° without solidifying. Globules of naphthalene (melting point 79°) were obtained still liquid at 40°.

When a liquid solidifies after having been thus cooled below its normal freezing point, the solidification takes place very rapidly, and is accompanied by a disengagement of heat often sufficient to raise its temperature from the point at which solidification begins up to its ordinary freezing point. This is well seen with crystallised hyposulphite of sodium ($S^2Na^2O^3$, $5H^2O$), which melts in its water of crystallisation at 45°, but when carefully cooled will remain liquid for a long time at the temperature of the atmosphere. If it be then caused to solidify, by agitation, or by throwing in a small fragment of the solid salt, the resulting rise of temperature is such as to be distinctly felt by the hand.

This phenomenon of continued liquidity, though seldom observed in so marked a degree as in the cases above mentioned, occurs so frequently to a less extent, that, when the temperature of transition from the solid to the liquid state or *vice versâ* is to be used as a mark of the chemical identity of a substance, it is much safer to determine the melting point than the freezing point, for the former temperature is not subject to variations of the same kind.

The following method is convenient for taking the melting points of substances in chemical investigations. Three or four glass tubes are drawn out till their sides become very thin and their bore nearly capillary, and into each is introduced a small quantity of the substance to be examined. They are then sealed at the bottom and placed in a beaker-glass containing water (or, if the substance melts above 100°, paraffin or sulphuric acid), and standing upon a small sand-bath by means of which its temperature can be slowly raised. The liquid is heated until the substance melts; then allowed to cool slowly to the point of solidification; it is then again warmed, and these operations are repeated, the temperatures of liquefaction and solidification being noted each time, until several closely concordant observations of each have been obtained, the means of which are the melting and solidifying points required.

Influence of Pressure upon Melting Points.—The variations which occur in the pressure of the atmosphere are without perceptible effect in altering the melting points of solids or freezing points of liquids, but greater differences of pressure are found to produce a very sensible effect. This was first observed by Prof. W. Thomson, who found that pressures of 8·1 and 16·8 atmospheres caused a lowering of the melting point of ice to the extent of 0·059° and 0·129° respectively. These results, therefore, verified the previous theoretical conclusions of Prof. J. Thomson, according to which an increase of pressure amounting to n atmospheres must lower the melting-point of ice by $t^\circ = n \,.\, 0{\cdot}0075^\circ$,—a formula which gives 0·061° and 0·126° as the differences of melting point corresponding to 8·1 and 16·8 atmospheres pressure. By a still greater pressure, Mousson (Ann. Ch. Phys. [3] lvi. 252) succeeded in maintaining water in the liquid state at 5 degrees below zero, and by a pressure estimated at 13,000 atmospheres he caused ice to melt at —18°. Analogous effects have been observed with other substances by Bunsen (Jahresber. über Chemie, u. s. w., 1850, 48) and Hopkins (*ibid.* 1854, 48). Their results are given in the following table. Bunsen considers that the observations of temperature in his experiments were correct within 0·1°, but that there may be an error of one or two atmospheres in the estimation of the pressures.

Freezing and Melting Points under increased Pressure.

Observer.	Hopkins.				Bunsen.			
Name of Substance.	Spermaceti.	Wax.	Sulphur.	Stearin.	Spermaceti.		Paraffin.	
Pressure in Atmospheres.	Melting point.				Pressure in Atmospheres.	Freezing point.	Pressure in Atmospheres.	Freezing point.
1	51·1°	64·7°	107·2°	67·2°	1	47·7°	1	46·3°
520	60·0	74·7	135·2	68·3	29	48·3	85	48·9
793	80·2	80·2	140·5	73·8	96	49·7	100	49·9
					141	50·5		
					156	50·9		

Latent Heat of Fluidity.—It has been pointed out already (p. 73) that the specific heats of solid bodies increase as they approach their melting points, and this fact has been connected with the increase of the coefficient of expansion which generally occurs simultaneously. In order to raise the temperature of a solid body 1 degree in the neighbourhood of its melting point, more heat is needed than would suffice to cause an equal rise of temperature at a lower part of the thermometric scale; in other words, of a given quantity of heat imparted to a body near its melting point, a larger proportion goes to produce molecular modifications (expansion, softening, &c.), and a smaller proportion to produce rise of temperature, than is the case at a lower part of the scale. From this point of view, it becomes quite conceivable that, at some particular temperature, depending on the nature of the substance under consideration, the whole quantity of heat communicated to a body might be expended in causing molecular changes (change of the state of aggregation, with or without change of volume, &c.), so that its effect in producing a rise of temperature would be imperceptible. This is exactly what takes place during the melting of solid bodies.

From these considerations we see that the phenomenon indicated in the second law of the passage from the solid to the liquid state of aggregation (p. 74), is one which attains its maximum degree of development at the point of actual liquefaction, but is the same in kind as what occurs at lower temperatures. We see also that the fusion of glass and other bodies which have no definite melting point, but in which liquefaction occurs gradually and extends over a greater or less interval of temperature, does not differ in any essential respect from the sudden melting of ice at the fixed temperature of 0° C. In the case of glass, a certain small proportion of the total quantity of heat imparted to it during its liquefaction, is expended in causing elevation of temperature; in the case of ice, this proportion is so small as to be imperceptible in comparison with that which goes to cause liquefaction.

It was formerly supposed that the temperature of a body was always proportional to the heat contained in it, and therefore that heat could not be communicated to a body without raising its temperature. The cessation of the rise of temperature during the fusion of solids was first observed by Black, while Professor of Chemistry in the University of Glasgow. He ascertained that, during this process, a considerable quantity of heat, different for different substances, disappears so far as the production of thermometric effects is concerned—or, as he expressed it, becomes *latent*—and that an equal quantity of heat appears during solidification. According to modern views, the expression *latent* (or hidden) *heat* is not strictly correct, for the effect of heat imparted to ice at the melting point is just as visible, though not the same, as that which it produces at other temperatures. Nevertheless, the expression is convenient from the fact of its being universally recognised and employed. The latent heat of fluidity is, then, the quantity of heat which must be imparted to one gramme of a solid at its melting point in order to melt it without raising its temperature, or which must be withdrawn from a liquid at its freezing point, in order to render it solid without lowering its temperature.

The following table gives the melting points and latent heats of fluidity, expressed in ordinary heat-units (gramme-degrees), of various substances, according to the determinations of Person (Ann. Ch. Phys. [3] xxvii. 250):—

Latent Heats of Fluidity.

Substance.	Melting Point.	Latent Heat.	Substance.	Melting Point.	Latent Heat.
Mercury	−39°	2·82	Tin	235°	14·25
Phosphorus	44	5·0	Silver	1000	21·1
Lead	332	5·4	Zinc	433	28·1
Sulphur	115	9·4	Chloride of calcium (CaCl. $3H^2O$)	28·5	40·7
Iodine	107	11·7			
Bismuth	270	12·6	Nitrate of potassium	339	47·4
Cadmium	320	13·6	Nitrate of sodium	310·5	63·0

The latent heat of water was found by Regnault and by Provostaye and Desains to be 79° C. According to Person, this number denotes the quantity of heat required to convert ice at 0° C. into water, but not the total quantity of the latent heat in the water, inasmuch as a certain additional portion of heat is rendered latent as the temperature of the ice rises from −2° to 0° (Ann. Ch. Phys. [3] xxx. 73). In six experiments on the fusion of ice previously cooled to between −2° and −21° C., the latent heat was found to vary between 79·9° and 80·1°, the mean quantity being 80°. Regnault also found greater values for the latent heat of water, as the ice had been cooled to a lower temperature. According to Hess, the true latent heat of water is 80·34° C. It has been proved by E. Desains (Ann. Ch. Phys. [3] lxiv. 419) that when water is cooled below 0° without freezing, the quantity of heat needed, in order to raise the temperature of a given weight from u° below zero to t° above zero, is the same whether the water remains liquid all the time, or whether it first freezes and afterwards melts again.

It is interesting to compare these values of the latent heat of water with those found by Black in 1762 (*Lectures on the Elements of Chemistry*, 2 vols. 4to. Edinburgh, 1803; vol. i. pp. 120–127). In one experiment, this philosopher measured the time required for the conversion of a known quantity of ice at 32° F. into water at 40° F. in a room of which the temperature remained constantly at 47° F., and compared it with the time during which the temperature of an equal weight of water rose under similar circumstances, from 33° F. to 40° F. He thus obtained for the latent heat of water the number 139° F., equal to 77·2° C. In another experiment, he melted 119 parts of ice at 32° F. by immersing it in 135 parts of water at 190° F., and so obtained 254 parts of water at 53° F. Hence, taking into account the different specific heats of the water and of the glass in which it was contained, he deduced the number 143° F., equal to 79·44° C.

The method adopted by Black in the second of these experiments is essentially the same as that still employed for the determination of latent heats of fluidity. A known weight of the substance to be examined is heated to a known temperature, and then immersed in the water (or other liquid) of a calorimeter, the temperature of which is such as to cause the substance to melt if solid, or, if liquid, to solidify; and when uniformity of temperature is established in the calorimeter, this temperature is determined. The experiment is therefore quite similar to the determination of the specific heat of a substance by the method of mixtures; the same apparatus may be used and the same precautions require to be taken in the two cases (see pp. 25–29).

In such an experiment let

A be the weight of water in the calorimeter, the water-equivalents of the calorimeter and thermometer supposed included;

W, the weight of substance operated upon;

t, the initial temperature of the calorimeter;
θ, the final temperature of the calorimeter;
T, the initial temperature of the substance;
$\mathfrak{C}$, its melting (or freezing) point;
C, the specific heat of the substance in the solid state between the temperatures $\mathfrak{C}$ and θ;
c, its specific heat in the liquid state between the temperatures T and $\mathfrak{C}$; and
L its latent heat of fluidity.

Suppose that the experiment is made upon a melted substance which gives out heat to the calorimeter and solidifies in it: then it is plain that the quantity of heat $A\,(\theta-t)$ absorbed by the calorimeter is made up of three parts—first, the heat lost by the substance in cooling from its original temperature to its freezing point; secondly, the heat given out by it during solidification; thirdly, the heat which it loses while cooling from its freezing point to the final temperature of the calorimeter. That is, $A\,(\theta-t) = W\,[c\,(T-\mathfrak{C}) + L + C(\mathfrak{C}-\theta)]$;

whence
$$L = \frac{A}{W}(\theta-t) - c(T-\mathfrak{C}) - C(\mathfrak{C}-\theta).$$

The manner in which this formula will require to be modified, in order that it may apply to the case of a solid substance which is melted in the calorimeter by absorbing heat from it, need not be specially pointed out.

Changes of Volume accompanying Fusion and Solidification.—The accelerated rate of expansion exhibited by most solids as they approach their melting points, is in most cases followed by a further expansion during the actual process of liquefaction, so that the melted substance occupies a greater bulk than the solid of the same temperature from which it is formed. This phenomenon has been particularly studied by Kopp (Ann. Ch. Pharm. xciii. 129), whose principal results are as follows:

Phosphorus (the yellow modification of specific gravity 1·826 at 10°), expands uniformly up to its melting point (44°), at which temperature its volume is 1·017 of what it was at 0°; when melted, its volume at the same temperature is 1·052 of the volume at 0°. Hence 100 vols. solid phosphorus at 44° become 103·4 vols. liquid phosphorus at the same temperature.

Sulphur (native crystals, specific gravity 2·069) expands irregularly near its melting point (115°). Its volume being 1 at 0°, is 1·010 at 50°; 1·037 at 100°; 1·096 at 115°; at the moment of fusion, the expansion amounts to 5 per cent., the volume then increasing to 1·150.

Wax (bleached bees'-wax, specific gravity 0·976 at 10°) expands very rapidly as it approaches its melting point (64°), but only 0·4 per cent. more at the moment of fusion. If the volume at 0° is 1, the volume at 50° is 1·068; at 60°, is 1·128; at 64°, is 1·161, and increases by fusion to 1·166.

Stearic acid (pure, specific gravity nearly 1·0 at 10°) expands less than wax before melting, but then expands as much as 11·0 per cent. The volume at 0° being 1, it is 1·438 at 50°; 1·055 at 60°; and 1·079 at 70°, at which temperature the acid melts, its volume increasing to 1·198.

Rose's fusible metal (2 pts. bismuth, 1 pt. tin, and 1 pt. lead; specific gravity 8·906 at 10°) expands, when heated from 0° to 59°, in the ratio of 1 to 1·0027; but contracts when further heated, its volume at 82° being equal to that at 0°, and at 95°, equal to 0·9947; in melting, between 95° and 98°, it expands by 1·55 per cent, so that at 98° its volume is equal to 1·0101. This alloy, therefore, contracts from 59° up to its melting point.

Water presents a remarkable exception to the general rule, and expands at the moment of fusion, or contracts on melting by about 10 per cent. One volume of ice at 0° gives 0·908 volume of water at the same temperature, or 1 volume of water at 0° gives 1·102 volume of ice. Dufour found, as the mean of 24 experiments, the density of ice at 0° equal to 0·9175, that of water at the same temperature being 1. Brunner found for the density of ice the number 0·918.

Solid hydrated salts, on the contrary, expand at the moment of fusion, *e. g.* chloride of calcium ($CaCl.3H^2O$), by 9·6 per cent; ordinary phosphate of sodium ($PNa^2HO^4.12H^2O$) and hyposulphite of sodium ($S^2Na^2O^3.5H^2O$) each by 5·1 per cent.

The expansion which takes place in water at the moment of solidification affords an explanation of several important phenomena. In the first place, it enables us to understand why increase of pressure should retard the freezing of water, instead of facilitating it, as it does that of most other liquids. Since the tendency of both heat and pressure is to diminish the bulk of water at 0°, and therefore to oppose the change of volume that occurs on freezing, it is easily conceivable that the one influence may (at least within certain limits) replace the other, and that a strong pressure applied to water at or below 0° may as effectually prevent its solidification, as the communication of heat which would raise its temperature above the freezing point. In the case of substances whose volume in the solid state is less than their volume in the liquid state, pressure acts in the opposite sense to heat, and therefore retards liquefaction and promotes solidification.

This same phenomenon is the cause of the powerful mechanical effects which occur when water freezes in a confined space. The bursting of water-pipes, and the breaking of jugs containing water, during frosty weather, are among the most familiar of these effects; and to these may be added the splitting of rocks by the freezing of water in their fissures and the swelling up of moist ground during frost.

The force with which water expands when cooled, and at the moment of becoming ice, is strikingly illustrated in the experiments made by Major Williams, at Quebec. Having filled a 13-inch iron bomb-shell with water, he closed the hole left for introducing the fusee by driving firmly in an iron plug weighing nearly 3lbs., and exposed it in this state to the frost. After some time, the iron plug was forced out with a loud explosion and thrown to a distance of 415 feet, and a cylinder of ice, 8 inches long, issued from the opening. In another experiment, the shell burst before the plug was driven out, and in this case a sheet of ice spread out all round by the crack. If we take into consideration the experiments of W. Thomson and Mousson already recorded (p. 75), it seems probable that some of the water must have remained liquid in these experiments, up to the moment when the resistance was overcome; that it then issued from the shell in the liquid state, but at a temperature below 0°, and therefore instantly began to solidify when the pressure was removed, and so retained the shape of the orifice whence it issued.

Bismuth, cast iron and antimony expand like water on becoming solid.

Solution of Solid Bodies in Water.—Very many solid substances are capable of dissolving in water, and thus forming with it a uniform mixed liquid. As a general rule, the solvent power of water increases with its temperature, but this is not universally the case; for example, chloride of sodium has very nearly the same solubility in cold water that it has in boiling water; lime-water saturated at 0°, contains nearly twice as much lime as can be dissolved by the same quantity of water at 100°. Several other calcium-compounds exhibit similar properties; thus the sulphate is more soluble in cold than in boiling water, and becomes quite insoluble in water between 140° and 150° (Cousté, Ann. des Mines, [5] v. 143). Sulphate of sodium is more soluble in water at 33° than at other temperatures, higher or lower, and has about the same solubility at 0° that it has at 100°. From the experiments of Sullivan (Rep. Brit. Association, 1859, p. 292) it appears that the solubility of very many salts attains a maximum at some particular temperature, above which it diminishes. Hence, perhaps, the reason why the solubility of most solids is commonly supposed to increase continuously as the temperature rises, is that it has been determined only at temperatures below 100°, and that the points of maximum solubility for most substances lie higher. If this be so, the solubility of sulphate of sodium,—and of the few other salts (selenate of sodium, sulphate of iron) in which similar properties have been observed,—is only in so far anomalous, that its temperature of maximum solubility is lower than that of most other substances. Water which is saturated at a given temperature with one substance can usually dissolve an additional quantity of another.

The liquefaction of solid bodies by solution in liquids, obeys essentially the same laws as their liquefaction by the direct application of heat. It is facilitated or retarded in the same way by great variations of pressure, and is attended by the absorption of a certain quantity of heat, which is evolved again when the dissolved substance separates from solution in the solid form; usually also the volume of the solution differs from the combined volumes of solid substance and water at the same temperature; and, lastly, solutions present the phenomenon of supersaturation, analogous to that of the deferred solidification of liquids.

As might be expected from the analogy with the liquefaction of solid bodies in general, increased pressure favours solution in cases where, as is usual, the volume of the water and dissolved substance is less after solution than the volume of the water and substance when separate; and diminishes the solubility of substances whose volume when dissolved is greater than their volume in the solid state, together with that of the water. (Comp. Sorby, Proc. Roy. Soc. xii. 538, also, Möller, Jahresber. 1862, pp. 11–13.)

The absorption of heat which occurs during solution is taken advantage of by the chemist for the artificial production of low temperatures. The table on the next page gives a few of the most frequently useful freezing mixtures, with the reduction of temperature which can be produced by means of each. In order to obtain the greatest possible effect by the use of any of these mixtures, it is necessary to use a considerable quantity of the materials (2 or 3 pounds at least); otherwise the whole heat required for the liquefaction is furnished by the containing vessel, and the whole of the mixture becomes liquid before its temperature has been much reduced. It is also of importance that the materials should be mixed as intimately as possible. Other more powerful freezing mixtures, depending on the employment of condensed gases, will be described hereafter.

Table of Freezing Mixtures.

Ingredients of the Mixture.	Parts by Weight.	Temperature produced, starting from 10°.	Diminution of Temperature.
Water	1	−16°	26°
Nitrate of ammonium	1		
Water	16	−12°	22°
Nitrate of potassium	5		
Chloride of ammonium	5		
Water	1	−19°	29°
Nitrate of ammonium	1		
Carbonate of sodium	1		
Snow, or pounded ice	5		20°
Chloride of sodium	2		
Snow, or pounded ice	1		45°
Crystallised chloride of calcium	2		
Crystallised sulphate of sodium	8	−20°	30°
Hydrochloric acid	5		

From a table already given (p. 60), it will be seen that water containing saline substances in solution freezes at a lower temperature than pure water, and that the depression of the freezing point increases with the quantity of substance in solution. This latter point is proved still more distinctly by the more recent experiments of Rudorff (Phil. Mag. [4] xxii. 552), from which it appears that the depression is very nearly in exact proportion to the quantity of salt dissolved. The ice which forms from a dilute solution of a salt yields nearly pure water when melted.

When a saturated solution is cooled, the excess of dissolved substance, beyond that which saturates the liquid at the lower temperature, generally separates out in the crystalline form; sometimes, however, especially if the solution is cooled slowly and is kept at perfect rest, a condition of unstable equilibrium may arise, like that of liquids cooled below their ordinary freezing points without solidifying, in which a greater quantity of substance is retained in solution than the liquid would be capable of dissolving if it were put in contact with it in the solid form. In this state, solutions are said to be supersaturated; and the same causes are in general sufficient to cause the separation of the excess of dissolved substance, as cause the solidification of over-cooled liquids.

If an aqueous solution of a salt is boiled in a flask of which the neck is drawn out to a fine point, and if the point is then hermetically sealed when all the air has been expelled, the solution very frequently remains supersaturated when cold; but on breaking the point, so as to readmit the air, even if this is done without shaking the solution in the least, or allowing the smallest fragment of glass to fall into it, crystallisation in most cases begins. If, however, the air that enters the flask has been previously passed through a red-hot tube, or even if it has been merely filtered through a column of cotton wool, crystallisation does not take place (comp. Loewel, Jahresber. 1852, p. 359; Schröder, Ann. Ch. Pharm. cix. 45; also particularly Gmelin's *Handbook*, i. 9–11). The most probable explanation of this difference is that the solid particles of soluble matter contained in the unheated or unfiltered air, disturb the molecular equilibrium of the solution by dissolving in it, and so cause crystallisation to begin. This explanation is confirmed by the fact that a supersaturated solution frequently does not crystallise if stirred with a glass rod or platinum wire which has been recently heated to redness, but crystallises instantly if touched with a rod that has lain long exposed to the air.

By cooling supersaturated solutions below 0°, they may be brought into such a condition, that either ice or the dissolved salt will crystallise out according to circumstances. Thus Rudorff found (*loc. cit.* and Pogg. Ann. cxvi. 55) that a small fragment of ice, thrown into a strongly cooled solution of platinocyanide of magnesium or sulphate of sodium, caused a crystallisation of ice, the whole of the salt remaining dissolved, until a very large proportion of the water had been transformed into ice; while a fragment of the solid salt thrown in caused the salt to crystallise, but no ice. The crystals of ice and of the salts used in these experiments were easily distinguishable by their different colours and specific gravities. These results are quite analogous to the simultaneous separate crystallisation of two or more salts contained in the same solution.

Vaporisation and Condensation.—When a quantity of water or alcohol is left exposed to the air, it gradually disappears, owing to its transformation into a transparent, invisible vapour, which diffuses into the atmosphere. This formation of vapour at the free surface of a liquid constitutes evaporation. It takes place more or less rapidly with all liquids, except some of those which are easily decomposed by heat when their temperature is sufficiently high. Some liquids, such as water, evaporate at all temperatures, but this is not the case with all: for instance, mercury gives off no sensible quantity of vapour at — 10°, and two basins may be placed near each other, under an exhausted receiver, at the ordinary temperature, one containing oil of vitriol and the other a solution of chloride of barium, without the smallest precipitate being formed in the latter. Some solid bodies, *e.g.* ice, iodine, camphor, give off vapour without previously passing into the liquid state; and it is proved by Regnault's experiments (upon benzene, bromide of ethylene, glacial acetic acid, chloride of cyanogen, and chloride of carbon), that substances which are capable of existing at the same temperature either as solids or liquids, produce, in both states of aggregation, vapours of equal tension (see next paragraph).

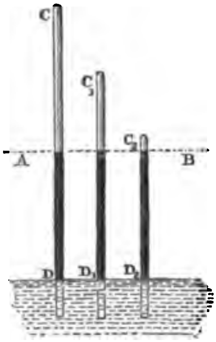
Fig. 539.

Fig. 540.

Tension of Vapours.—The quantity of any given liquid which can evaporate in an enclosed space, either previously vacuous or already containing a gas or vapour, is limited, and depends on the nature of the liquid, on the temperature, and on the extent of the enclosed space. When the liquid is in excess, that is, when some of it remains after the formation of the largest quantity of vapour that is possible under the circumstances, evaporation ceases when the vapour exerts a certain pressure upon the sides of the containing vessel. The laws of evaporation are, therefore, most easily arrived at by studying, in the first instance, the phenomena of the formation of vapour in a vacuum, in which case the pressure exerted by the vapour itself is the only one to which the sides of the vessel are exposed.

If a glass tube, closed at one end. about a yard long and three-quarters of an inch wide, is filled with mercury and inverted in a basin of that liquid, as shown in *fig.* 539, a vacuous space, about six inches in length, is formed at the top of the tube. On now passing up a drop or two of ether or alcohol into this space, the liquid will immediately evaporate, so that the surface of the mercury and of the tube will remain dry, but the mercury column will be depressed by the elastic force of the vapour which has been formed. The amount of this elastic force, or of the pressure which the vapour exerts upon the sides of the tube and upon the top of the column of mercury, is evidently measured by the difference between the height of this column and that of the barometer at the time of the experiment. On transferring the tube in this condition to a mercury-trough provided with a deep cylindrical well (*fig.* 540), and depressing it slightly, the space occupied by the vapour above the mercury will be diminished; the tension of the vapour will therefore increase, and the mercury column A C will be still further depressed. But on continuing to diminish in this way the volume of the vapour, a point will soon be reached at which part of it returns to the liquid state and condenses as a dew upon the inside of the tube and on the mercury; and if the height of the column A C be measured, as soon as the first trace of condensed liquid becomes visible, it will be found to remain the same until the tube has been depressed so far that the whole of the vapour has been converted into liquid, and the tube becomes filled with mercury, surmounted by a drop of liquid ether or alcohol. The progress of the experiment in this stage will be easily understood from *fig.* 541, where C D represents the tube when the liquid first begins to appear in the space above the mercury, and A B the level of the mercury in the tube above that in the trough. As the tube is depressed successively to the positions $C_1 D_1$, and $C_2 D_2$, more and more of the vapour is liquefied, but the remaining portion exerts neither more nor less pressure than the quantity which existed in the tube at the instant when liquefaction first began to take place; and hence the surface of the mercury remains immovably at the level A B. Again, if the tube is raised up out of the mercury, the top of the mercury column will still remain at the level A B, until the whole of the liquid has again evaporated into the space above it, but from this point it will begin to rise higher and higher as the tube is still further raised; if, however, when the tube has attained its highest position (so that the open end is only just covered by the mercury in the trough), an additional quantity of ether or alcohol is passed up into it, the column of mercury will sink; and if the quantity of liquid passed up is more than can evaporate in the portion of the tube unoccupied by the mercury, the surface of the latter will sink again to the level A B (*fig.* 541).

Fig. 541.



These experiments prove that when a vapour is compressed, its temperature remaining always the same, its elastic force increases up to a certain limit which it cannot exceed, the effect of any further compression being to change it to a liquid; and that when a vapour is in contact with any portion of the corresponding liquid, in a space otherwise vacuous, its elastic force always attains this limit, whatever may be the relative volumes of vapour and liquid. In this condition, a vapour is said to be saturated, or to exert its maximum tension.

Maximum Tension.—The maximum tension which the vapour of any liquid can exert depends upon the nature of the liquid, and upon its temperature.

If we pass up into the first of three barometric tubes, like that represented in *fig.* 539, a small quantity of ether, into the second some alcohol, and into the third some water, taking a larger quantity of each liquid than can evaporate completely within the tube, the mercury column will be depressed to a different level in each, supposing all three to have the same temperature. If, for instance, the temperature is 10° C., the mercury will be depressed about 11¼ inches in the first tube, nearly 1 inch in the second tube, and a little more than ⅓ inch in the third.

If the three tubes are now gradually heated, by surrounding them with warm water or otherwise, more vapour will be formed from the liquid contained in each of them; the elastic force or tension of each vapour will accordingly increase, and the mercury will descend lower and lower in the tubes as the temperature rises. At about 35°, the tension of the ether-vapour will have become equal to that of the atmosphere, and hence at this temperature, the mercury in the tube containing it will have been driven down so as to be at the same level as that in the reservoir; at about 78·5° the same will be the case with the mercury in the alcohol-tube; and at about 100° with that contained in the water-tube.

When a saturated vapour is cooled, the pressure upon it remaining unaltered, complete liquefaction takes place, just as it does when the pressure is increased and the temperature remains the same. The condition of saturation, or maximum tension, is therefore a limiting condition, beyond which a vapour can neither be compressed nor cooled without returning to the state of liquid.

On the other hand, when a saturated vapour not in contact with an excess of liquid is heated, it ceases to be saturated (unless the pressure upon it is increased at the same time to a corresponding extent). Hence, when a further quantity of liquid is brought in contact with a vapour which has been thus heated, more vapour is formed in the same space, until saturation is again produced, and the tension increases at the same time till it reaches the maximum tension corresponding to the higher temperature.

Distinction between Vapours and Gases.—It has been already stated, that when the space into which a liquid can evaporate is increased until the whole quantity of liquid has become vapour, the tension of the vapour diminishes with any further increase of volume; and that when a vapour, not in contact with the liquid from which it is formed, is compressed, its tension augments until liquefaction begins. In proportion as a vapour under these conditions is expanded, its tension becomes more and more nearly inversely proportional to the volume which it occupies; that is, its properties approach more and more nearly to those of a perfect gas. Similarly, when a saturated vapour, not in contact with an excess of liquid, is heated, its elastic force increases, and it expands if the pressure upon it is not proportionably augmented; and as the temperature rises, the relation between the tension or elastic force, p, of the vapour, its volume, v, and its temperature, t, comes to be more and more nearly expressed by the equation

$$pv = J(a + t);$$

which, as we have already seen (p. 45), expresses the relation between these three quantities in the case of a perfect gas (see also p. 50).

Hence the physical properties of vapours, when sufficiently expanded, and at sufficiently high temperatures, are identical with those of the permanent gases.

From this it is natural to conclude, conversely, that the so-called permanent gases themselves are only vapours which, at ordinary pressures and temperatures, are very far removed from their points of saturation, and that by exposing them to lower temperatures and increasing the pressure, a point might be reached for each of them, at which the pressure would be equal to the maximum tension which it was capable of exerting at the temperature of the experiment, and therefore, that any further diminution of temperature or increase of pressure would cause it to become liquid. This conclusion has been actually verified in the case of many gases formerly regarded as permanent, the only gases which have hitherto resisted all attempts to liquefy them being hydrogen, oxygen, nitrogen, nitric oxide, carbonic oxide and marsh-gas. (The methods employed for the liquefaction of gases will be further considered in connection with the processes adopted for obtaining great reductions of temperature.)

Tension of Vapours in presence of Permanent Gases.—The familiar fact of the evaporation of water in the open air affords sufficient proof that the presence of a permanent gas in any given space does not prevent volatile liquids giving off vapour into the same space. By measuring the volume and elastic force of a given quantity of dry air, or other gas, then introducing a little more of any liquid than can completely evaporate in it, and when equilibrium has been re-established, again measuring the volume and elastic force of the mixture of gas and vapour, the tension of the latter can be ascertained. In this way it has been found that, when the liquid exerts no solvent or chemical action upon the gas, the combined tension of gas and vapour is nearly equal to the separate tension of the gas, increased by the maximum tension which the vapour is capable of exerting in an otherwise vacuous space at the temperature of the experiment. In other words, the vapour given off by a liquid at any temperature has nearly the same maximum tension, whether it is formed in a space previously vacuous or filled with a permanent gas. The only essential difference between the evaporation of a liquid in a vacuum, and its evaporation in a gas, is that, in the former case, the vapour attains the condition of saturation in an inappreciably short time, while in the latter, this condition is arrived at more slowly. Regnault's experiments (Mém. Acad. Sciences, xxvi.) prove, however, that liquids do not give off vapour of quite so great a tension in a space occupied by a permanent gas, as they do in a vacuum, and that the difference increases as the temperature rises.

Boiling Points.—Ebullition.—From the facts stated in the last paragraph, it follows that the temperature at which the vapour of a liquid introduced into the barometric vacuum would exert sufficient elastic force to drive the mercury down to the bottom of the tube, so as to make it stand at the same level inside and outside, is also the temperature at which the vapour formed on heating the liquid in the air would exert an elastic force equal to the atmospheric pressure. As already stated, the first of these effects is produced by ether-vapour at 35°, by alcohol at 78·5°, and by water at 100°; these temperatures, however, are those at which the liquids respectively boil when heated in the open air, the barometer being at its average height. The boiling point of a liquid is, therefore, the temperature at which the tension of its vapour becomes equal to the atmospheric pressure. This temperature is evidently not absolutely constant for each liquid, but varies more or less with alterations of the pressure of the atmosphere. A liquid at its boiling point is in a limiting condition, comparable to that of a saturated vapour; any diminution of pressure or increase of temperature equally causes it to pass from the liquid to the vaporous state. The two conditions are in fact conterminous; and the temperature at which a liquid produces vapour of any given maximum tension, is also the temperature at which the liquid would boil under an atmospheric pressure equal to that tension. Hence the observation of the pressures under which a liquid boils at various temperatures constitutes a method of determining the maximum tension of its vapour at those temperatures.

The phenomenon of ebullition, which presents itself when heat is applied to the lower part of a mass of liquid, already at such a temperature that the tension of its vapour is equal to the pressure of the atmosphere, results from the transformation of the liquid into vapour at the points where the heat is applied, and the escape of this vapour in the form of bubbles through the superincumbent liquid.

The temperatures at which different liquids boil, under the ordinary atmospheric pressure, vary very greatly. They will be found given for each liquid in the article of this dictionary wherein it is specially described; in the following table a few boiling points are given in order to illustrate the range of temperature through which they occur.

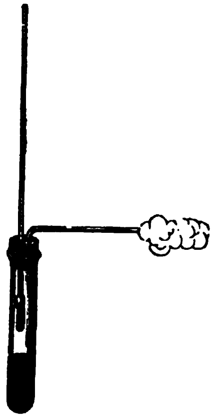
Table of Boiling Points.

Liquid.	Boiling Point.	Pressure in millimetres of mercury.	Authority.
Nitrous oxide . .	−87·9°	759	Regnault
Carbonic anhydride .	−78·2	767·3	„
Ammonia . . .	−33·7	749·3	Bunsen
Sulphurous anhydride	−10·5	744	„
Chloride of ethyl .	+11·0	758	Pierre
Oxide of ethylene .	13·5	746·5	Wurtz
Aldehyde . . .	19·8	734	Kopp
Ether . . .	34·2	742	„
Sulphide of carbon .	47·9	755·8	Pierre
Methylic alcohol .	61·0	754	Delffs
Bromine . . .	63·0	760	Pierre
Alcohol . . .	78·4	760	Gay-Lussac
Benzene . . .	80·4	752	Kopp
Water . . .	100·0	760	„
Acetic acid . .	116·9	750	„
Cymene . . .	177·5	744	„
Naphthalene . .	216·8	747·6	„
Phosphorus . .	290	. .	Pelletier
Oil of vitriol . .	325	. .	
Mercury . . .	350	. .	Regnault
Sulphur . . .	440	. .	Dumas; Deville and Troost
Cadmium . . .	860	. .	Deville and Troost
Zinc	1040	. .	„

Determination of Boiling Points.—The boiling points of different liquids being among their most characteristic properties, the determination of them becomes a very frequent and important operation in chemical research. The method recommended by Kopp, in order to ensure as much accuracy as possible in these observations, is as follows:—

The liquid to be examined is placed in a cylindrical glass vessel, containing a few scraps of freshly ignited platinum foil, the diameter of which, when the quantity of liquid is small, need not much exceed that of the bulb of the thermometer. This vessel is closed by a cork, through the centre of which the thermometer is inserted, in such a way that it can be raised or lowered, so that the bulb may dip either into the liquid or merely into the vapour. It is generally advisable to give the thermometer the latter position, since, as will be seen by what follows, the temperature of the liquid may, under circumstances which not unfrequently occur, rise somewhat above the true boiling point; but even when this is the case, a thermometer in the vapour will show the real boiling point of the liquid: under nearly all circumstances, the thermometer will stand lower in the vapour than it does in the liquid, if this is a mixture of two or more liquids of different boiling points instead of a pure, homogeneous substance. Through a second hole in the cork is inserted a glass tube, open at both ends, and bent at a right angle, as shown in *fig.* 542; by connecting this tube with a condenser, the loss of the liquid used for the experiment can be prevented. The liquid is heated either by applying a small flame to the outside of the vessel, or by means of a water-bath or sand-bath, care being taken that the sides of the vessel above the liquid do not get over-heated. The indications of the thermometer are observed during the whole time that the liquid is being slowly boiled away, until only a small quantity remains. The temperature thus observed is not, however, in most cases, the true boiling point of the liquid: usually, part of the mercury column in the thermometer rises above the cork, and is therefore exposed to a lower temperature than that of the boiling liquid; consequently, the upper extremity of the column stands at a lower point than it would do if the thermometer were completely immersed in the liquid. In order to find the correction which it thus becomes necessary to apply, a second thermometer is placed so that its bulb is in contact with the stem of the thermometer inserted into the cork of the boiling vessel, and is half way between the top of the mercury column of the latter thermometer and the middle of the cork. The temperature indicated by this second thermometer may be taken as the mean temperature of that portion of the mercury column of the principal thermometer which is not heated by the vapour of the boiling liquid. Let this temperature be t°; let the uncorrected boiling point, directly indicated by the principal thermometer, be T°; let N be the difference between T and the point of the scale situated at the middle of the cork, that is to say, the length, expressed in degrees of the scale, of that portion of the mercury column of the principal thermometer of which the mean temperature is t°; lastly, let δ be the coefficient of apparent expansion of mercury in the glass of which the thermometer is constructed. The correction to be applied to the directly observed temperature T° is then

Fig. 542.



$$= N(T-t)\,\delta.$$

As already stated (p. 57), δ may always be taken, in calculating the value of this expression, as $= 0{\cdot}0001545$.

The table which follows on p. 86 gives the amounts of the correction in question for various values of N and of $T-t$. The amounts corresponding to other values of these factors can be easily deduced by interpolation from the numbers given in the table.

This table sufficiently shows that the correction in question can never be neglected in accurate experiments, and that in the case of liquids of high boiling points, its value may become very considerable.*

Since the boiling point of a liquid depends on the pressure to which the liquid is subjected, another correction becomes necessary in order to reduce determinations made under the varying pressure of the atmosphere, to the values which would be found if the atmosphere exerted always its normal pressure, equal to that of 760 millimetres of mercury at 0°. Strictly speaking, the correction to be applied to the boiling point of a liquid observed under an atmospheric pressure differing by a given amount from the above standard pressure, varies with the nature of the liquid; since equal alterations of pressure do not cause precisely equal changes in the boiling points of different liquids. Nevertheless, the greatest variations which ever occur in the pressure of the atmosphere are relatively so small, that they may, without any appreciable error, be regarded as affecting the boiling points of all liquids equally: to the extent, namely, of 0·1° for a variation of pressure of 2·7 millimetres of mercury, this number being deduced from direct determinations of the boiling point of water under different pressures.

In what follows, whenever the boiling point of a liquid is spoken of without further explanation, it is to be understood to mean the boiling point under a pressure equal to that of 760 millimetres of mercury at 0°.

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* It is obvious that a precisely similar correction ought to be applied to all thermometric observations in which any portion of the mercury in the stem of the thermometer is at a different temperature from that in the bulb.

Table for the Correction of Boiling Points. (Kopp.)

$T - t$	*N*																			
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200
10	0·02	0·03	0·05	0·06	0·08	0·09	0·11	0·12	0·14	0·15	0·17	0·18	0·20	0·22	0·23	0·25	0·26	0·28	0·29	0·31
20	·03	·06	·09	·12	·15	·18	·22	·25	·28	·31	·34	·37	·40	·43	·46	·49	·52	·56	·59	·62
30	·05	·09	·14	·18	·23	·28	·33	·37	·42	·46	·51	·55	·60	·65	·70	·74	·79	·83	·88	·92
40	·06	·12	·18	·25	·31	·37	·43	·50	·56	·62	·68	·74	·80	·86	·92	·99	1·05	1·11	1·17	1·23
50	·08	·15	·23	·31	·38	·46	·53	·62	·70	·77	·85	·92	1·00	1·08	1·16	1·23	1·31	1·39	1·46	1·54
60	·09	·18	·28	·37	·46	·56	·65	·74	·83	·92	1·01	1·11	1·20	1·29	1·39	1·48	1·57	1·66	1·76	1·85
70	·11	·22	·33	·43	·53	·65	·76	·87	·97	1·08	1·19	1·29	1·40	1·51	1·62	1·72	1·83	1·94	2·05	2·16
80	·12	·25	·37	·50	·62	·74	·87	·99	1·11	1·23	1·36	1·48	1·60	1·72	1·85	1·97	2·09	2·22	2·34	2·46
90	·14	·28	·42	·56	·70	·83	·97	1·11	1·25	1·39	1·52	1·66	1·80	1·94	2·08	2·22	2·36	2·49	2·63	2·77
100	·15	·31	·46	·62	·77	·92	1·08	1·23	1·39	1·54	1·69	1·85	2·00	2·16	2·31	2·46	2·62	2·77	2·93	3·08
110	·17	·34	·51	·68	·85	1·01	1·19	1·36	1·52	1·69	1·86	2·03	2·20	2·37	2·54	2·71	2·88	3·05	3·22	3·39
120	·18	·37	·55	·74	·92	1·11	1·29	1·48	1·66	1·85	2·03	2·22	2·40	2·59	2·77	2·96	3·14	3·33	3·51	3·70

Circumstances which modify the Boiling Point.—Although, when a liquid is heated in such a manner that vapour can escape freely from some part of its surface, the vapour so formed has a tension equal to the pressure upon the free surface of the liquid as soon as the temperature of the latter reaches the boiling point, this temperature may nevertheless be attained, and even considerably exceeded, without the formation of a trace of vapour, if no portion of the surface of the liquid is freely exposed. These conditions can be realised by suspending the liquid to be examined in a second liquid of equal specific gravity, but higher boiling point.

The phenomena which take place under these circumstances have been particularly studied by **Dufour** (Ann. Ch. Phys. [3] lxviii. 378). In order to examine them in the case of water, he employed a mixture in the requisite proportions of oil of cloves (previously heated alone to about 200°) and linseed oil. The water, already heated to 80° or 90°, was dropped gently into the mixture of oils, so as not to disturb the film which coated the bottom of the vessel, and the temperature of the bath was gradually raised. Under these circumstances the ordinary boiling point of water, 100°, was passed without the occurrence of any perceptible change, and traces of ebullition scarcely began to show themselves below 110° or 115°. Even at these temperatures, ebullition seldom began except when the globules of water came in contact with the sides of the vessel or with the thermometer. A burst of vapour then occurred, and the globule, more or less diminished in size, was driven rapidly away, like a pith ball after touching an electrified conductor. These contacts were of course more difficult to avoid in the case of large than of small globules; hence the latter remained liquid, as a rule, to higher temperatures than the former.

In these experiments, it was a rare exception when ebullition occurred between 100° and 110°; very commonly globules of 10 mm. in diameter reached 120° or 130°, and in one experiment the last temperature was attained by a globule of 18 mm. diameter, and therefore containing more than 3 c.c. of water. Spheres of 10 or 12 mm. diameter often reached 140°; those of 5 or 6 mm. reached 165°; and others of from 1 to 3 mm. attained 175° or even 178°, temperatures at which the elastic force of the vapour which forms at the freely exposed surface of water is between 8 and 9 atmospheres.

At these high temperatures, the contact of a solid body very generally occasioned the sudden partial or complete vaporisation of the globules, accompanied by a hissing sound like that produced on immersing red-hot iron in water. This invariably occurred when the globules were touched with pieces of wood or chalk, shreds of cotton, paper, &c., but not always on contact with a glass rod or metallic wire, the difference appearing to depend on the porous structure of the former substances. A platinum wire appeared to lose, to some extent, by frequent usage, the power of causing sudden vaporisation.

Sudden ebullition, amounting even to an explosion, if the temperature was above 120°, invariably occurred on passing the discharge of a Leyden jar or induction coil through a globule. A similar, but less violent, effect was produced by the passage of a weak galvanic current. These results are attributed by **Dufour** less to the contact of the globules with the conducting wires, than to the disengagement of gas at the extremities of the latter.

Saturated aqueous solutions of various salts—for example, chloride of sodium, sulphate of copper, nitrate of potassium, &c.—also remained liquid at temperatures much above their boiling points, when immersed in melted stearic acid resting on a layer of melted sulphur. In like manner, globules of chloroform (boiling point 61°), suspended in a solution of chloride of zinc, often remained liquid up to 97° or 98°; and globules of liquid sulphurous anhydride (boiling point $-10{\cdot}5°$) could be heated in diluted sulphuric acid as high as $+8°$. In all these cases, the same causes that operated in the case of water, sufficed to occasion the sudden complete or partial conversion of the overheated globules into vapour.

These results throw important light upon the nature of ebullition, and seem to indicate that it is to some extent an accidental phenomenon. In order to understand them, we must remember that, the globules being surrounded on all sides by liquid, evaporation cannot go on at their surface in the ordinary way. They are, however, in a state of tension, or unstable equilibrium, such that a very slight cause may occasion the sudden formation of vapour of more than the atmospheric tension. The most effectual of such causes would obviously be the contact of a minute globule of air or other gas: this globule, however small, would be a space into which vapour could be given off, and this vapour, having an elastic force greater than the pressure (that of the atmosphere and the upper layers of the liquid) whereby the globule was prevented from expanding, would force back the liquid walls of the bubble of gas, suddenly converting it into a large bubble of steam. Hence the unfailing efficacy, in causing the ebullition of the overheated globules of liquid, of the passage of an electric current or the contact of porous substances, such as chalk, wood, paper, &c., which either allow air to escape from their pores when immersed in the heated liquid, or carry down into it small globules of air adhering to them. These globules afford space for the *commencement* of the formation of vapour, and this process being once begun, the space is increased by the force of the vapour already formed within it. In the absence of any such space, the liquid globule is in a condition somewhat analagous to that of a drop of melted glass which has been suddenly cooled in water (Rupert's drops), and which falls to powder on receiving the smallest scratch: there is no reason why the formation of vapour should begin at one point of the mass rather than at another, and thus the whole remains in a state of molecular tension until something occurs at some particular point to weaken the effect of the forces which oppose the formation of vapour, or until the tension increases (in consequence of rise of temperature) to such a degree that these forces are overcome simultaneously throughout the whole mass. It will be seen further on that these considerations exactly agree with the explanation which the mechanical theory of heat affords of the passage from the liquid to the gaseous state.

Even when liquids are heated in open vessels, the occurrence of ebullition, or the formation of vapour in the *interior* of the mass, appears to depend on like accidental causes. Thus the influence of the nature of the vessel wherein a liquid is contained has been long recognised. It has been observed, for instance, that water, which will boil steadily at 100° in a metallic vessel, may often be heated to 105° or 106° without boiling, in a glass vessel previously washed with strong sulphuric acid. Under these circumstances, ebullition generally takes place very irregularly: at a certain temperature a sudden burst of vapour occurs, and the temperature of the liquid falls at the same time to nearly the normal boiling point; the liquid then remains tranquil for a time, until the temperature having again risen considerably, another burst of vapour takes place, and so on. The "bumping" of heated liquids which results from this intermittent formation of vapour, is familiar to every chemist. It may be prevented to some extent by putting into the liquid a few scraps of platinum, or a globule of mercury; a small piece of charcoal is, however, much more effectual than either of these, though not always admissible. This irregular ebullition occurs much more frequently in some liquids than others, and to a greater extent in certain glass vessels than in others. For instance, methylic alcohol (boiling point 61°) may show a difference in its temperature of ebullition amounting, according to Kopp, to 5 or 6 degrees, depending on the vessel in which it is examined. When a liquid is boiling steadily in a glass flask or retort, it may almost always be noticed that the bubbles of vapour start from one or two particular points of the surface of the glass, indicating the existence of some irregularity of the glass at those points favourable to the formation of vapour. Another illustration of the necessity of some other cause than mere temperature in order to bring about the ebullition of liquids, is afforded by the remarkable observation of Professor Donny, of Ghent, that water thoroughly deprived of air and sealed up in a rather long glass tube quite free from air, may be heated to 138° at one end of the tube without boiling, and is then suddenly and violently thrown to the other end by a burst of vapour. An additional fact of the same kind may sometimes be observed during the distillation of liquids under the ordinary pressure. The writer has occasionally seen a liquid distil very rapidly, thus showing that vapour was being formed rapidly at the surface, although ebullition could not be maintained by the use of a more powerful flame than that which had sufficed, at an earlier stage of the experiment, to boil a larger quantity of the same liquid.

The whole of these phenomena cease to be unintelligible if, with Dufour, we distinguish between the boiling point of a liquid, and the temperature at which the elastic force of its vapour becomes equal to the pressure of the atmosphere, and define the boiling point as the lowest temperature at which ebullition *can* occur, instead of as the temperature at which, under normal conditions, it *must* occur.

Spheroïdal State.—When a drop of water is allowed to fall upon a piece of iron, the temperature of which considerably exceeds 100°, it retains its globular form, moves about rapidly on the surface of the iron without wetting it, and evaporates with comparative slowness. As the iron cools, a point is reached at which the globule of water wets it, spreads over its surface, boils and quickly disappears. The condition of the globule first described has been distinguished as the spheroïdal state. This condition can be assumed by all volatile liquids when they come in contact with the surface of either a solid or a liquid body heated considerably above their boiling points. The temperature of a liquid in the spheroïdal state is always below its ordinary boiling point, notwithstanding the higher temperature of the surface on which it rests. The absence of ebullition is therefore due in this case to some other cause than that which produces the phenomena of deferred ebullition which were considered in the last paragraph. It is the result of a want of perfect contact between the liquid and the heated surface. Many experiments prove that the liquid globule rests upon a sort of cushion of its own vapour, produced by the heat radiated from the hot surface against its under side. As fast as this vapour escapes from under the globule, its place is supplied by a fresh quantity produced in the same way, so that the globule is constantly buoyed up by it, and never comes into actual contact with the heated surface. If, however, the temperature of the latter is allowed to fall, the formation of vapour becomes less and less rapid, until at last it is not supplied fast enough to prevent the globule touching the hot metal or liquid on which it rests: as soon as contact occurs, heat is rapidly imparted to the globule, it enters into ebullition, and quickly boils away.

According to Boutigny's experiments, the lowest temperature at which a metallic vessel will cause the spheroïdal state to be assumed by water is 142°; for alcohol the lowest temperature is 134°, and for ether 61°.

Solid bodies which evaporate without becoming liquid also assume a condition analogous to the spheroïdal state of liquids, when they are placed upon a surface whose temperature is sufficiently high to vaporise them very rapidly. This is very distinctly seen on throwing a piece of solid carbonate of ammonium into a red-hot platinum crucible, and when a fragment of solid carbonic anhydride is placed upon any good conducting surface at the ordinary temperature.

Effect of Substances in Solution on the Boiling Point of Liquids.—Liquids holding solid bodies in solution boil generally at higher temperatures than they do in the pure state. On the other hand, the boiling point of water is lowered by mixing it with alcohol, and that of alcohol by mixing it with ether; the boiling point of a mixture being always intermediate between the boiling points of its components. The effect of salts in raising the boiling point of water may be considered as also coming under this rule. The following table gives the boiling points of saturated solutions of several salts, according to Legrand.

Table of Boiling Points of Saturated Saline Solutions.

Salt.	Weight of salt dissolved in 100 parts of water.	Boiling Point.	Salt.	Weight of salt dissolved in 100 parts of water.	Boiling Point.
Acetate of potassium .	798·2	169°	Tartrate of potassium .	296·2	114·7°
Nitrate of calcium .	362·2	151	Chlorate of potassium .	61·5	104·2
Carbonate of potassium	205·0	135	Chloride of sodium .	41·2	108·4
Acetate of sodium .	209·0	124·4	Phosphate of sodium (dried)	112·6	106·6
Nitrate of sodium .	224·8	121	Carbonate of sodium .	48·5	104·6
Chloride of strontium .	117·5	117·8	Chloride of barium .	60·1	104·4
Nitrate of potassium .	335·1	115·9			
Chloride of ammonium	88·9	114·2			

(For Legrand's determinations of the boiling points of weaker solutions of these and some other salts, and for the similar experiments of Griffiths and Faraday, see Gmelin's *Handbook*, i. 269, 270.)

Very contradictory opinions have been maintained by different observers with regard to the temperature of the vapour which issues from boiling saline solutions. It has been said, on the one hand, to be the same as that of pure water boiling under the same pressure; and, on the other hand, to be equal to that of the highest stratum of the solution. According to the recent experiments of Magnus (Pogg. Ann. cxii. 408), the latter statement appears to be nearest the truth. These experiments prove decisively that the vapour of boiling solutions is hotter than that of pure water, and that its temperature rises as the solutions become more concentrated, and therefore boil at higher temperatures; nevertheless, the vapour was always found a little colder than the mass of the boiling solution, and the difference was greater at high temperatures than it was at low ones.

Relations between the Boiling Point of substances and their Chemical Composition.—Many attempts have been made to trace some connection between the boiling points of different liquids and their chemical composition. The most extensive and important series of observations that have been made upon this point are due to Kopp (Ann. Ch. Pharm. xcvi. 2, 330; xcviii. 267, 367; Phil. Trans. 1860, 257). The principal conclusions deducible from these investigations are as follows:—

1. Analogous compounds, presenting the same difference of composition, very frequently differ by the same amount in their boiling points, or the interval between their boiling points is proportional to their difference of composition. A compound containing xC more or less than another of analogous function, generally boils at a

temperature $x \times 29$ degrees higher or lower than the latter, and if it contains xH more or less it commonly boils at $x \times 5$ degrees lower or higher. A particular instance of the application of this rule is to homologous compounds: in the homologous acids $C^nH^{2n}O^2$ (ACIDS, i. 50), and in the corresponding alcohols and compound ethers, the addition of CH^2 to the formula of a compound raises its boiling point on an average by 19°, agreeing with the above rule.

2. An acid, $C^nH^{2n}O^2$, boils at a temperature 40° higher than the alcohol, $C^nH^{2n+2}O$ (ALCOHOLS, i. 97), the oxidation of which may give rise to the acid.

3. A compound ether (ETHERS, ii. 512), $C^nH^{2n}O^2$, boils at a temperature 82° lower than the acid, $C^nH^{2n}O^2$, isomeric with it.

If we start from the boiling point of ethyl-alcohol, = 78°, these three propositions enable us to calculate the boiling points of a large number of organic substances, alcohols, acids, and compound ethers, represented by the above general formulæ. The following tables serve to show how far the boiling points thus calculated correspond with those actually observed.

Boiling Points of Alcohols, $C^nH^{2n+2}O$.

Name.	Formula.	Calculated Boiling Point.	Observed Boiling Point.
Methylic alcohol .	CH^4O	59°	Kane, 60°; Delffs, 60·5°; Kopp, 65°; Pierre, 66°; Dumas and Péligot, 66·5°.
Ethylic alcohol .	C^2H^6O	78	Dumas and Boullay, 76°; Gay-Lussac, Pierre, Kopp, Delffs, Andrews, 78°.
Tritylic alcohol .	C^3H^8O	97	Chancel, 96°.
Tetrylic alcohol .	$C^4H^{10}O$	116	Wurtz, 109°.
Amylic alcohol .	$C^5H^{12}O$	135	Pasteur, 127°—129°; Cahours, Pierre, Kopp, Delffs, 132°; Rieckher, 135°.
Hexylic alcohol .	$C^6H^{14}O$	154	Faget, 148°—154°.
Heptylic alcohol .	$C^7H^{16}O$	173	Städeler, 177°—177·5°.
Cetylic alcohol .	$C^{16}H^{34}O$	344	Favre and Silbermann, 366°?

Boiling Points of Acids, $C^nH^{2n}O^2$.

Name.	Formula.	Calculated Boiling Point.	Observed Boiling Point.
Formic acid . .	CH^2O^2	99°	Liebig, 99°; Bineau, Favre and Silbermann, 100°; Kopp, 105°.
Acetic acid . .	$C^2H^4O^2$	118	Delffs, 116°; Kopp, 117°; Sébille-Auger, 119°; Dumas, 120°.
Propionic acid .	$C^3H^6O^2$	137	Dumas, Malaguti, and Leblanc, about 140°; Limpricht, Kopp, 142°.
Butyric acid . .	$C^4H^8O^2$	156	Kopp, Delffs, 156°; Pierre, 163°; Pelouze and Gélis, about 164°.
Valeric acid . .	$C^5H^{10}O^2$	175	Dumas and Stas, Delffs, 175°; Kopp, 176°.
Caproic acid . .	$C^6H^{12}O^2$	194	Brazier and Gossleth, Wurtz, 198°; Fehling, 202°—209°.
Œnanthylic acid .	$C^7H^{14}O^2$	213	Städeler, 218°.
Caprylic acid . .	$C^8H^{16}O^2$	232	Fehling, 236°; Perrot, 238°.
Pelargonic acid .	$C^9H^{18}O^2$	251	Perrot, 225°; Cahours, 260°.

In other groups of compounds, a difference of CH^2 in the composition of analogous substances corresponds frequently to a nearly constant difference of boiling point: but this difference sometimes amounts to more than 19 degrees, and sometimes to less. For instance, in the series of hydrocarbons C^nH^{2n-6}, homologous with benzene, C^6H^6, a difference of CH^2 in composition corresponds to an average difference of about 24° in boiling point; in the series of alcohol-radicles (or hydrides) C^nH^{2n+2}, homologous with ethyl, C^2H^{10}, (or marsh-gas, CH^4) the difference of boiling point corresponding to the same difference of composition, is also nearly 24°; in the series of acetones $C^nH^{2n}O$, it is about 22°. On the other hand, the difference of boiling point, corresponding to a difference of CH^2 in composition, is less than 19° in the anhydrides

Boiling Points of Compound Ethers, $C^nH^{2n}O^2$.

Name.	Formula.	Calculated Boiling Point.	Observed Boiling Point.
Formate of methyl .	$C^2H^4O^2$	36°	Kopp, Andrews, 33°; Liebig, 36°—38°.
Acetate of methyl . Formate of ethyl .	$C^3H^6O^2$	55	Andrews, 55°; Kopp, 56°; Dumas and Péligot, 58°. Liebig, Delffs, 53°; Kopp, 55°; Löwig, 56°.
Acetate of ethyl . .	$C^4H^8O^2$	74	Dumas and Boullay, Pierre, Kopp, Delffs, 74°.
Butyrate of methyl Acetate of trityl . Formate of tetryl . Propionate of ethyl	$C^5H^{10}O^2$	93	Favre and Silbermann, Delffs, 93°; Kopp, 95°; Pierre, 102°. Berthelot, about 90°. Wurtz, about 100°. Kopp, 96°—98°; Limpricht and Uslar, 101°.
Valerate of methyl. Butyrate of ethyl . Acetate of tetryl . Formate of amyl .	$C^6H^{12}O^2$	112	Kopp, 114°—115°. Pelouze, 110°; Delffs, 113°; Kopp, 115°; Pierre, 119°. Wurtz, 114°. Delffs, 114°; Kopp, about 116°.
Valerate of ethyl . Butyrate of trityl . Acetate of amyl .	$C^7H^{14}O^2$	131	Delffs, 132; Otto, Kopp, Berthelot, 133°—134°. Berthelot, about 130°. Cahours, 125°; Kopp, Delffs, 133°.
Caproate of ethyl . Propionate of amyl	$C^8H^{16}O^2$	150	Lerch, 120°; Fehling, 162°. Wrightson, about 155°.
Butyrate of amyl . .	$C^9H^{18}O^2$	169	Delffs, 173°—176°.
Valerate of amyl . Acetate of capryl .	$C^{10}H^{20}O^2$	188	Kopp, 188; Balard, about 196°. Dachauer, 191—192°; Bouis, 193°.
Pelargonate of ethyl Caproate of amyl .	$C^{11}H^{22}O^2$	207	Cahours, 216°—218; Delffs, 224°. Brazier and Gossleth, 211°.
Laurostearate of ethyl	$C^{14}H^{28}O^2$	264	Görgey, 264°; Delffs, 269°.

$C^{2n}H^{4n-2}O^3$, homologous with acetic anhydride, $C^4H^6O^3$ (namely, about 12·5°); in the ethers of the acids $C^nH^{2n-2}O^4$, homologous with oxalic acid, $C^2H^2O^4$ (namely, about 14°); also in the carbonates, sulphocyanates and borates of the alcohol-radicles C^nH^{2n+1}.

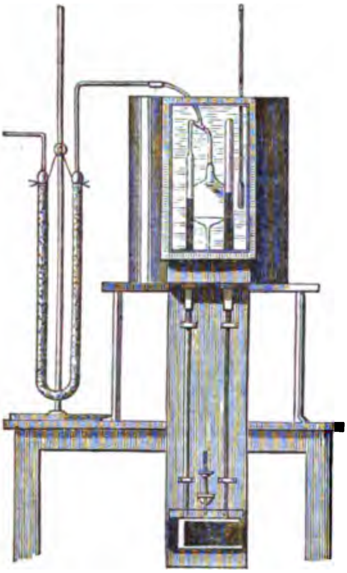
These results seem to show that, as a rule, the greater the quantity of oxygen contained in any series of compounds, the smaller is the effect on the boiling point of a difference of composition amounting to CH^2.

In the chlorides, bromides and iodides of the alcohol-radicles C^nH^{2n+1}, a difference in composition of CH^2 causes a difference in boiling point of from 24 to 31 degrees; in the corresponding sulphides and sulphydrates (mercaptans) the difference also considerably exceeds 19°.

Measurement of the Tension of Vapours.—The various methods that have been employed for measuring the maximum tension of vapours at different temperatures, depend upon principles already explained. We have here to describe briefly the manner in which these principles were put in practice, and to state the most important results obtained.

The tension of vapours at temperatures below the ordinary boiling points of the corresponding liquids, and therefore at pressures less than that of the atmosphere, have been measured by determining the depression of the mercury column of a barometer produced by the saturated vapours at known temperatures. *Fig.* 543 represents the apparatus employed by Regnault (*Relation des Expériences*, &c. p. 469) in his principal series of experiments made by this method. The liquid whose vapour is to be examined is contained in a small bulb almost completely filled by it, and hermetically sealed without any trace of air. This bulb is introduced into a glass globe, the neck of which is then drawn out, bent at a right angle, and cemented into a narrow T-tube of copper, the other branches of which communicate, one of them through a drying tube containing pumice-stone and sulphuric acid, with an air-pump, the other, by a capillary tube, with the top of a wide glass tube open below and dipping into mercury. This last tube forms the barometer, the depressions of which are observed; its upper part is inside a metal water-bath, one face of which is formed by a sheet of plate glass, and in which are also contained the upper part of an ordinary barometer, to serve as a standard of comparison, and the glass globe spoken of above; this, as shown in the figure, rests on a metal ring carried by a support rising from the bottom of the bath. Previous to beginning the experiments, the inside of the glass globe and of the tubes communicating with it is rendered absolutely dry by repeatedly pumping out the air, and each time allowing it to be filled again by air dried by passing through the sulphuric acid drying tube. Then, by bringing a piece of hot charcoal near the outside of the globe, the bulb containing the liquid is burst, and the experiments are proceeded with by observing simultaneously the temperature of the bath in which the globe is immersed, and the difference in height of the two barometers.

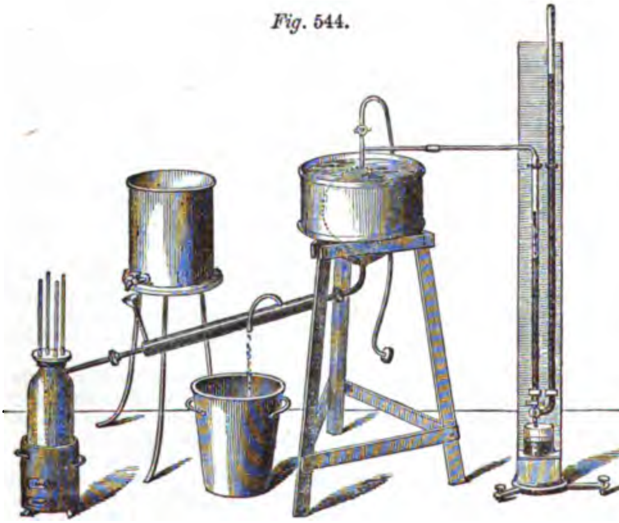
Fig. 543.



The same apparatus, slightly modified, served for the determination of the tension of vapours in presence of air or other gases.

For the determination of the tension of the vapour of water at higher temperatures, **Regnault** (*ibid.* p. 515) employed the apparatus represented in *fig.* 544, an apparatus which enabled him to measure the pressure under which water boiled at various temperatures (see p. 83). The apparatus consists of a copper retort, containing the water to be experimented upon, and communicating, through a tube surrounded by cold water (whereby the steam produced is condensed and whence it continually flows back as water into the retort), with a copper globe of 24 litres capacity. This globe is connected with a manometer which indicates the pressure inside the whole apparatus, and also with a branch tube by means of which air can be withdrawn from or forced into the apparatus, so as to bring the pressure to the required amount. The temperature of the boiling water in the retort is indicated by four thermometers, two of which dip into the water, and two into the steam. In order to prevent any alteration in the capacities of the bulbs of the thermometers, resulting from the pressure of the vapour upon them, they are enclosed in iron tubes, closed at the bottom and containing mercury.

Fig. 544.



The following table gives the results obtained at intervals of five degrees between

− 32° and + 230°. (For tables of the tensions of water-vapour at each degree centigrade between these limits, and at each tenth of a degree between −10° and +35° and between 85° and 101°, see **Regnault**, *loc. cit.* pp. 624–633.)

Maximum Tension of Water-vapour between −32° *and* +230°. (**Regnault.**)

Temperature.	Tension, millimetres.	Temperature.	Tension, millimetres.	Temperature.	Tension, millimetres.
−32°	0·320	55°	117·478	145°	3125·55
30	0·386	60	148·791	150	3581·23
25	0·605	65	186·945	155	4088·56
20	0·927	70	233·093	160	4651·62
15	1·400	75	288·517	165	5274·54
10	2·093	80	354·643	170	5961·66
5	3·113	85	433·041	175	6717·43
0	4·600	90	525·450	180	7546·39
+ 5	6·534	95	633·778	185	8453·23
10	9·165	100	760·000	190	9442·70
15	12·699	105	906·410	195	10519·63
20	17·391	110	1075·370	200	11688·96
25	23·550	115	1269·410	205	12955·66
30	31·548	120	1491·280	210	14324·80
35	41·827	125	1743·880	215	15801·33
40	54·906	130	2030·280	220	17390·36
45	71·391	135	2353·730	225	19097·04
50	91·982	140	2717·630	230	20926·40

Determinations of the tension of water-vapour up to 111 degrees have also been made by **Magnus** (Pogg. Ann. lxi. 225) by a method essentially similar to the first of those above described. His results agree closely with those of Regnault. (For the older determinations of the pressure of steam at high temperatures by **Arago** and **Dulong**, see Gmelin's *Handbook*, i. 262.)

The following table, by **Fairbairn** and **Tate** (Phil. Trans. 1860, p. 220), gives the temperatures at which water is completely converted into saturated steam under various pressures, together with the volume of steam formed under these circumstances compared with that of the water from which it is produced.

Pressure, Temperature, and Volume of Saturated Steam.

Pressure.		Temperature.		Volume.
Inches.	Millimetres.	Fahrenheit.	Centigrade.	
5·35	135·9	136·77°	58·20°	8275·3
8·62	219·9	155·33	68·51	5333·5
9·45	240·0	159·36	70·76	4920 2
12·47	316·7	170·92	77·18	3722·6
12·61	320·2	171·48	77·49	3715·1
13·62	345·9	174·92	79·40	3438·1
16·01	406·6	182·30	83·49	3051·0
18·36	466·3	188·30	86·83	2623·4
22·88	581·2	198·78	92·66	2149·5
53·61	1361·7	242·90	117·16	943·1
55·52	1410·1	244·82	118·23	908·0
55·89	1419·6	245·22	118·45	892·5
66·84	1697·7	255·50	124·16	759·4
76·20	1935·4	263·14	128·41	649·2
81·53	2070·8	267·21	130·67	635·3
84·20	2138·9	269·20	131·77	605·7
92·23	2342·6	274·76	134·86	584·4
90·08	2287·9	273·30	134·05	543·2
99·60	2529·8	279·42	137·45	515·0
104·54	2655·2	282·58	139·21	497·2
112·78	2864·6	287·25	141·80	458·3
122·25	3105·1	292·53	144·74	433·1
114·25	2901·9	288·25	142·36	449·6

The following tables contain the results of some of Regnault's experiments on the tension of the vapours of other liquids. (Mém. Acad. Sciences, xxvi. 349–658.)

Tension of Vapours.

Temperature.	Alcohol.	Ether.	Sulphide of carbon.	Chloroform	Benzene.	Oil of turpentine.
° C.	mm.	mm.	mm.	mm.	mm.	mm
− 20	3·3	67·5	43·5	. .	4·9	
10	6·6	113·3	81·0	. .	13·4	
0	12·8	183·3	132·0	. .	26·6	2·1
+ 10	24·3	286·4	203·0	. .	46·6	2·9
20	44·5	433·3	301·8	160·5	76·3	4·4
40	133·6	909·6	617·0	366·2	182·3	10·8
60	350·3	1728·5	1163·7	751·0	388·6	26·5
80	812·8	3024·4	2033·8	1404·6	756·6	61·3
100	1694·9	4950·8	3329·5	2426·5	1352·3	131·1
120	3219·7	7702·2	5145·4	3916·2	2256·3	257·2
140	5637·0	. .	7556·9	5965·8	3537·0	464·0
150	7258·7	. .	. .	7226·5	4336·7	605·2

Tension of Vapours—continued.

Liquefied Gases.				Mercury.			
Temperature.	Sulphurous anhydride.	Ammonia.	Sulphydric acid.	Temperature.	Tension.	Temperature.	Tension.
° C.	mm.	mm.	mm.	° C.	mm.	° C.	mm.
− 78·2	. .	240·0	441·4	0	0·0200	120	1·534
40	. .	528·6	. .	10	·0268	150	4·266
30	287·5	876·6	2808·6	20	·0372	180	11·00
20	479·5	1397·7	4273·0	30	·0530	200	19·90
10	762·5	2149·5	5945·0	40	·0767	250	75·75
0	1165·1	3162·9	7709·3	50	·1120	300	242·1
+ 10	1719·5	4612·2	10896·3	60	·1643	350	663·2
20	2462·0	6467·0	14151·5	70	·2410	400	1587·9
30	3431·8	8832·2	18035·3	80	·3528	450	3384·3
40	4670·2	11776·4	22582·5	90	·5142	500	6520·2
50	6220·0	. .	27814·8	100	·7455	520	8264·9

It was supposed by Dalton that the tension of the vapours of all liquids is the same at temperatures equally distant from their respective boiling points. The observations from which the above tables are constructed show that this rule is not strictly true, but is nearly so in most cases for small intervals of temperature above or below the boiling points: hence, in order to correct boiling point observations for the variations of atmospheric pressure, it may be assumed without sensible error that a difference of pressure equal to 2·7 millimetres of mercury causes a difference in the boiling points of all liquids, equal to that which it produces in the case of water,—namely, 0·1° C. (see pp. 85 and 92.)

Tension of the Vapours of Mixed Liquids and of Saline Solutions.—Regnault's experiments on the tension of the vapour of mixed liquids prove that: (1) when two liquids exert no solvent action upon each other, as *water* and *sulphide of carbon*, water and *bichloride of carbon* (CCl^4), or water and *benzene*, the tension of the vapour which rises from a mixture of them is very nearly equal to the sum of the tensions of the two separate liquids at the same temperature; (2) with water and ether, which dissolve each other to some extent, but not in all proportions, the tension of the vapour of the mixture is much less than the sum of tensions of the separate liquids, being scarcely equal to that of ether only; (3) when the two liquids dissolve each other in all proportions, as ether and sulphide of carbon, benzene and alcohol, water and alcohol, the tension of the vapour of the mixed liquid is intermediate between the tensions of the separate liquids.

The tension of the vapour of saline solutions has been examined by Regnault and by Wüllner (Jahresber. 1858, 42–47; 1860, 47–49). Regnault's experiments were made by means of the apparatus represented in *fig.* 543, p. 92; Wüllner employed a differently arranged apparatus, but one which depended on essentially the same principles. It results from these investigations that the tension of the vapour of a solution is less than that of the vapour of pure water at the same temperature, and that in the case of efflorescent salts and of salts that are permanent in the air, the diminution of the tension of the vapour emitted by the solution is exactly proportional to the quantity of salt dissolved in a constant weight of water, but in the case of deliquescent salts it is proportional to the quantity of hydrated salt dissolved: *e. g.*, for a solution of potash, to the quantity of $KHO.2H^2O$; for a solution of soda, to the quantity of $NaHO.1\frac{1}{2}H^2O$; for a solution of chloride of calcium, to the quantity of $CaCl.3H^2O$. The absolute amount of diminution of tension depends on the temperature, and becomes greater as the temperature rises.

Tension of Vapours in an unevenly heated space.—In an enclosed space, the temperature of which is different at different parts, the vapour of a liquid can assume a state of statical equilibrium only when its tension is equal to the maximum tension corresponding to the temperature of the coldest part of the space. If the vapour has, to begin with, a greater tension than this, liquefaction will take place in the coldest part, since the pressure is greater than that which the vapour can support at the temperature of this part, and this process will continue until the tension throughout the whole space is reduced to the point already stated. It is upon this principle that the process of distillation, and the action of the condenser of the steam engine, depend.

Complete Vaporisation of Liquids under great pressures.—When the temperature of a liquid is raised sufficiently high, vaporisation occurs under the highest pressure to which the substance can be subjected. Alcohol, ether, or rock-oil, enclosed in a tube of strong glass or iron, is completely converted into vapour only when the space not occupied by the liquid is somewhat greater than the volume of the liquid itself. With rock-oil the empty space may be somewhat smaller than with alcohol, and with ether still less. Alcohol when thus heated acquires increased mobility, expands to twice its original volume, and is then suddenly converted into vapour. This change takes place at 207° C. (404·6° Fah.), when the alcohol occupies just half the volume of the tube; if the tube is more than half filled with alcohol, it bursts when heated. A glass tube one-third filled with water becomes opaque when heated, and bursts after a few seconds. If this chemical action of the water on the glass be diminished by the addition of a little carbonate of soda, the transparency of the glass will be much less impaired; and if the space occupied by the water be ¼ of the whole tube, the liquid will be converted into vapour at about the temperature of melting zinc (Cagniard de la Tour).—If liquid carbonic anhydride sealed in a glass tube occupies $\frac{18}{30}$ of the volume of the tube at 0°, it neither increases nor diminishes in bulk when heated, because the increase of volume produced by heating is just compensated by the diminution caused by vaporisation. If it occupies ⅓ of the space at 0°, its volume diminishes when it is heated, and increases when it is cooled, because the loss by evaporation preponderates over the expansion. If it takes up ⅔ of the space, its volume increases by heat and contracts by cold, as in a thermometer; but at + 30° (86° Fah.) the whole is converted into vapour. The gas, which at 0° occupies the space above the liquid carbonic anhydride would, if condensed, yield $\frac{1}{13}$ of its volume of liquid acid; and that which is produced at + 30° would give ⅓ (⅔? Gmelin) of its volume of liquid carbonic anhydride at 0°. (Thilorier.)

When chloride of ethyl was heated in a very thick sealed tube, the upper surface ceased to be distinctly marked at about 170°, and was replaced by an ill defined nebulous zone possessing no reflecting power; as the temperature rose, this zone increased in width in both directions, becoming at the same time more and more transparent. After a time, the liquid was entirely converted into vapour, and the tube became quite transparent and apparently empty. As the temperature fell, the same phenomena were reproduced in the opposite order (Drion, Ann. Ch. Phys. [3] lvi. 33). Similar appearances were observed on heating ether in a sealed tube to about 190°. According to Drion, the temperature at which ether is completely vaporised, in a space nearly three times its original volume, is 190·5°. The precise temperatures observed in these experiments are, however, of no real significance, unless they are accompanied by accurate determinations of the corresponding real volumes of the liquid and vapour.

It has been similarly observed by Andrews that when liquid carbonic anhydride was gradually heated to 31°, the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished, or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 31° no apparent liquefaction of carbonic anhydride or separation into two distinct forms of matter could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave similar results. (Andrews, in Miller's *Chemical Physics*, ed. 1863, pp. 328, 329.)

Latent Heat of Vaporisation.—When heat is imparted to a volatile liquid, its effect is, at most temperatures, twofold. Part of it goes to increase the temperature of the liquid, and part to cause vaporisation. But when a liquid is boiling under constant pressure, however much heat is communicated to it, the whole of it is absorbed in producing the second of these effects only. Conversely, when heat is withdrawn from a saturated vapour, under a pressure which is maintained constant, the vapour is changed into a liquid, without alteration of temperature. The consumption of heat in vaporisation, without the production of a corresponding elevation of temperature, and its evolution during condensation, unaccompanied by a corresponding fall of temperature, were first observed by Black. These phenomena were described by him by saying that during the former process, a certain quantity of sensible heat became latent, and that this latent heat became sensible again during condensation. The quantity of heat that must be given to a liquid to convert it into vapour, or which must be withdrawn from a vapour to convert it into liquid, without causing change of temperature, is still spoken of as the latent heat of vaporisation.

The determination of this quantity is made by determining the specific heat of the substance for an interval of temperature within which it passes from the liquid to the vaporous state, or *vice versâ*, and is therefore in principle similar to the determination of the latent heat of fluidity (p. 77). The following table gives the number of units of heat which must be imparted to a unit of weight of various liquids at their respective boiling points, in order to convert them into vapours at the same temperatures. The letters F S in the third and sixth columns denote that the determinations were made by Favre and Silbermann (Ann. Chim. Phys. [3] xxxvii. 464–470); the letter A denotes determinations by Andrews (Chem. Soc. Qu. J. i. 27); and Rg, by Regnault.

Latent Heat of Vapours.

Substance.	Latent Heat of Vapour.	Observers.	Substance.	Latent Heat of Vapour.	Observers.
Water . . .	535·77	F S	Valeric acid . .	103·52	F S
„ . . .	535·90	A	Butyric acid . .	114·67	„
„ . . .	536·67	Rg	Acetate of ethyl .	105·80	„
Bromine . .	45·60	A	„ „ .	92·68	A
Trichloride of phosphorus	51·42	„	Acetate of methyl .	110·20	„
Sulphide of carbon . .	86·67	„	Formate of ethyl .	105·30	„
Tetrachloride of tin	3·053	„	Formate of methyl	117·10	„
Alcohol . . .	208·92	F S	Iodide of ethyl .	46·87	„
„ . . .	202·40	A	Iodide of methyl .	46·07	„
Methylic alcohol .	263·86	F S	Oxalate of ethyl .	72·72	„
„ „ .	263·70	A	Butyrate of methyl	87·33	F S
Amylic alcohol .	121·37	F S	Ethal . . .	58·44	„
Ether . . .	91·11	„	Oil of turpentine .	68·73	„
„ . . .	90·45	A	Terebene . .	67·21	„
Amylic ether . .	69·40	F S	Oil of lemons .	70·02	„
Acetic acid . .	101·91	„	Hydrocarbons from amylic alcohol:		
Formic acid . .	120·72	„	(*a*). (B. P. 205°)	59·91	„
			(*b*). (B. P. 250°)	59·71	„

The latent heat of vaporisation varies with the temperature at which the vapour is formed; more heat is for instance required to convert a given quantity of water at 50° into vapour of the same temperature than to produce the same change in water at 100°. It was supposed by Watt that the latent heat of vaporisation diminished exactly at the same rate as the sensible heat increased, so that the sum of the two remained constant at all temperatures. But Regnault (*Relation des Expériences*, &c., pp. 635—728; also *Works of the Cavendish Society*, vol. i. p. 294) has shown that this is not the case. He finds that the total quantity of heat λ (expressed in heat-units) which a unit of weight of saturated aqueous vapour contains at the temperature t° C., exceeds the amount contained in the same weight of water at 0° by the quantity

$$\lambda = 606{\cdot}5 + 0{\cdot}305\,t.$$

If from this we subtract the quantity of heat which a unit of weight of water at t° contains, beyond that which is contained in the same weight of water at 0° (see Regnault's determinations of the specific heat of water at different temperatures, p. 34), we shall obtain the latent heat L of the vapour of water at the temperature $t°$. The values of λ and L for various temperatures are given in the next table, together with the tensions expressed in millimetres and atmospheres.

Latent Heat of Water-Vapour.

Temperature.	Tension.		λ	L.
	mm.	atm.		
0° C.	4·60	0·006	606·5	606·5
50	91·98	1·121	621·7	571·6
100	760·00	1·000	637·0	536·5
150	3581·23	4·712	652·2	500·7
200	11688·96	15·380	667·5	464·3
230	20926·40	27·535	676·6	441·9

The following formulæ represent in like manner the results of Regnault's determinations (Mém. Acad. Sciences, xxvi. 881) of the total heats of vaporisation of several other substances at various temperatures:

Sulphide of carbon: $\lambda = 90{\cdot}0 + 0{\cdot}14601\,t - 0{\cdot}0004123\,t^2$.
Ether: $\lambda = 94{\cdot}0 + 0{\cdot}4500\,t - 0{\cdot}0005555\,t^2$.
Benzene: $\lambda = 109{\cdot}0 + 0{\cdot}2443\,t - 0{\cdot}0001315\,t^2$.
Chloroform: $\lambda = 67{\cdot}0 + 0{\cdot}1375\,t$.
Perchloride of carbon (CCl^4): $\lambda = 52{\cdot}0 + 0{\cdot}1463\,t - 0{\cdot}000172\,t^2$.
Acetone: $\lambda = 140{\cdot}5 + 0{\cdot}3664\,t - 0{\cdot}000516\,t^2$.

The following table gives the total heats of vaporisation of some additional liquids at the temperatures at which they boil under the ordinary atmospheric pressure (*ibid.* 913):

Substance.	Boiling Point.	Total Heat of Vaporisation.	Substance.	Boiling Point.	Total Heat of Vaporisation.
Alcohol . . .	78·26°	265·52	Bromine . . .	60°	50·95
Amylic alcohol . .	132	211·78	Chloride of tin .	114	46·84
Oil of lemons . .	174·80	160·49	Chloride of arsenic .	133	69·74
Oil of turpentine . .	159·15.	139·15	Trichloride of phosphorus .	73·80	67·24
Petrolene . . .	. .	194·87	Acetate of ethyl .	74	154·49
Chloride of ethyl . .	12·50	97·70			
Iodide of ethyl . .	71	58·95			

Regnault finds, as the result of direct experiments (*ibid.* 903), "that the total heat of vaporisation of a liquid in a current of gas is equal to that which the same liquid absorbs when it boils in an atmosphere formed by its own vapour, and exerting an elastic force equal to that actually acquired by the vapour of the liquid in the current of gas."

Cold produced by Vaporisation. Liquefaction of Gases.—When the evaporation of a liquid is hastened by reducing the pressure upon it and continually removing the vapour which forms, or by exposing a large surface and rapidly renewing the atmosphere in contact with it, the consequent absorption of heat is such, in the case of the more volatile liquids, as to produce a very considerable fall of temperature. Water, for instance, may be frozen by placing it under the exhausted receiver of an air-pump near a vessel of strong sulphuric acid (Leslie). The rapid volatilisation of more volatile liquids produces still more striking results, and in fact constitutes the most effectual means known of producing extremely low temperatures.

By causing a rapid stream of dry air from the bellows of a glass-blowers' lamp to bubble by several tubes at once through about 200 grammes of ether, Loir and Drion (Bull. Soc. Chim. Paris, i. 184; Séance du 22 Juin, 1860) succeeded in reducing the temperature of the liquid to −34° in 4 or 5 minutes, and maintaining this temperature very nearly constant for at least 15 or 20 minutes. At this temperature considerable quantities of *cyanogen* can be condensed at the atmospheric pressure. The condensation of this gas begins under these circumstances at about −22°; by blowing gently on the surface of the condensed liquid with a common pair of bellows it is immediately caused to solidify. By similar means, *sulphurous anhydride* is easily liquefied. *Chlorine* does not condense under the common pressure at −34°, but by using liquid sulphurous anhydride in place of ether, a temperature of −50° can be produced, and this is amply sufficient for the liquefaction of both chlorine and *ammonia*. Lastly, by evaporating liquid ammonia (which boils in the air at −35·7°) in an exhausted receiver over sulphuric acid, they attained the temperature of about −87°, at which point the ammonia solidified, and *carbonic anhydride* condensed to a liquid at the common atmospheric pressure.

An apparatus for the liquefaction of ammonia, to be used for refrigeration, has been described by **Regnault** (Mém. Acad. Sciences, xxvi. 609), and a very simple contrivance for the same purpose was exhibited by **Carré** at the International Exhibition in London in 1862. (For a description and figure of the last apparatus, see Miller's *Chemical Physics*, ed. 1863, p. 298, footnote.)

Several gases can be liquefied by increased pressure alone, without reducing their temperature below that of the atmosphere. The necessary pressure can often be attained by evolving the gas in an enclosed space (as in a sealed glass tube); under these circumstances, the elastic force continues to increase until the point of maximum tension is reached, and then liquefaction occurs. In this way, carbonic anhydride may be liquefied by its own pressure when it is evolved from acid carbonate of sodium and diluted sulphuric acid in a strong wrought iron bottle connected with a wrought iron receiver. When the liquid carbonic anhydride thus produced is allowed to escape in a fine stream into the air, part of it is immediately vaporised, and the consequent absorption of heat is sufficient to cause the remainder to condense to a white, crystalline solid, like snow. The principle of this method was first put in practice by **Faraday** in experiments on the small scale; an apparatus in which considerable quantities of liquid carbonic anhydride could be thus prepared was first devised and constructed by **Thilorier**.

The pressure necessary for the liquefaction of gases may also be produced by compressing them by means of a force-pump, as in **Natterer's** apparatus for the liquefaction of nitrous oxide.

By the evaporation of gases, condensed by any of the processes above indicated, the lowest temperatures yet attained can be produced, the greatest degree of cold hitherto recorded being −140°, the temperature, according to Natterer, of a mixture of liquid nitrous oxide and bisulphide of carbon evaporating *in vacuo*.

Still more powerful means of liquefaction than those already mentioned, were employed by **Faraday** in his later experiments on this subject (Phil. Trans. 1845, p, 170), and he thereby succeeded in reducing to the liquid state all known gases, with the exception of oxygen, hydrogen, nitrogen, nitric oxide, carbonic oxide, and marsh-gas, —and in solidifying the greater number of them. The method adopted was to subject the gases to the joint action of powerful mechanical pressure and extreme cold. The first object was attained by the successive action of two air-pumps, the first having a piston one inch in diameter, the second only half an inch. The first produced a pressure of about 20 atmospheres, the second increased it to upwards of 50. The tubes into which the gas thus condensed was made to pass were of green bottle-glass, from ⅙ to ¼ of an inch in external diameter, and had a curvature in one portion of their length adapted for immersion in a freezing mixture. The mixture employed consisted of solid carbonic anhydride and ether. The cold produced by it amounted to −76·6° in the open air, and to −110° under the exhausted receiver of the air-pump.

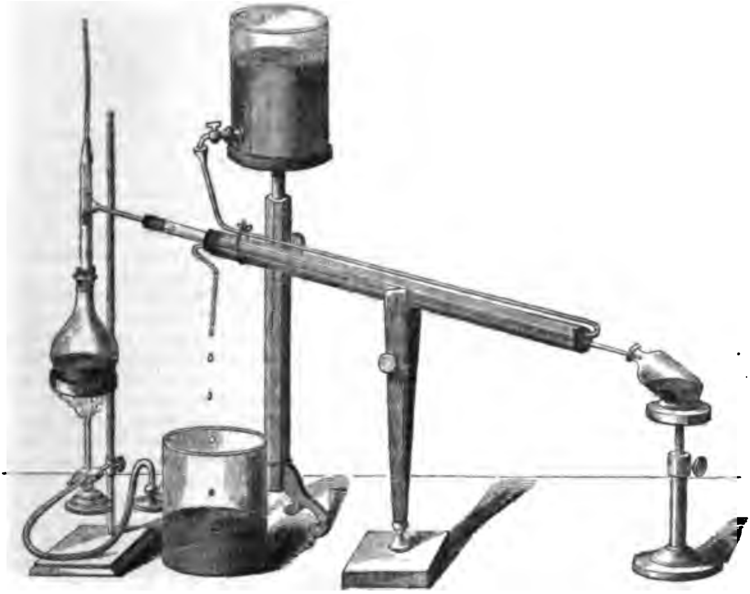
Many gases, when subjected to this extreme degree of cold, were liquefied without the use of the condensing apparatus: this was the case with chlorine, cyanogen, ammonia, sulphuretted hydrogen, arseniuretted hydrogen, hydriodic acid, hydrobromic acid, carbonic anhydride, ethylene, nitrous oxide, and oxide of chlorine. Fluoride of silicon liquefied at a pressure of 9 atmospheres. The following were solidified when subjected to the action of the carbonic anhydride bath *in vacuo:* hydriodic acid, hydrobromic acid, sulphurous anhydride, sulphuretted hydrogen, carbonic anhydride, oxide of chlorine, cyanogen, ammonia, and nitrous oxide. The following gases did not solidify, even at the lowest temperature that could be obtained: ethylene, fluoride of silicon, fluoride of boron, phosphoretted hydrogen, hydrochloric acid, and arseniuretted hydrogen. The six gases mentioned at the commencement of the preceding paragraph showed no signs of liquefaction when cooled by the carbonic anhydride bath *in vacuo:* hydrogen and oxygen at 27 atmospheres, nitrogen and nitric oxide at 50, carbonic oxide at 40, and marsh-gas at 32 atmospheres.

Andrews has since succeeded in exposing these gases to still greater pressures, but without producing liquefaction, although a bath of ether and solid carbonic anhydride was used; air was reduced to $\frac{1}{675}$ of its bulk, oxygen to $\frac{1}{554}$, hydrogen to $\frac{1}{500}$, carbonic oxide to $\frac{1}{278}$, and nitric oxide to $\frac{1}{350}$ of its original volume. Hydrogen and carbonic oxide departed less from Boyle's law than oxygen and nitric oxide.

Distillation. — One of the processes most frequently resorted to by the chemist for the purpose of separating different substances is to expose the mixture containing them to a temperature at which the constituent it is wished to isolate rises in vapour, while the others remain still solid or liquid. The ordinary methods of performing this operation of distillation, and the apparatus commonly employed are too familiar to every chemist for it to be necessary to describe them here in detail. (For a full description of the process and the modifications that become desirable in particular cases, the reader is referred to *A Handbook of Chemical Manipulation*, by C. Greville Williams, London, 1857, pp. 202–244.)

When the liquid submitted to distillation is a mixture of two or more substances of unequal volatility, the vapour formed when ebullition begins generally contains a larger percentage of the most volatile constituent than the liquid remaining in the retort. Hence, the composition of the liquid alters as the distillation continues, and its boiling point rises accordingly. On the other hand, if the boiling point of a liquid remains constant during distillation, it is usually an indication that its composition is unaltered by the process, and therefore that the composition of the distillate also continues the same throughout. The boiling point of a liquid becomes therefore a very useful indication of the uniform or varying nature of the products of its distillation, and by collecting apart the portions which pass over at different temperatures, a mixture of different liquids may often be to a great extent resolved into its constituents. It seldom happens, however, except with a mixture of two liquids whose boiling points are very distant from each other, that a single operation of this kind gives either constituent in a state of purity. This is especially the case when the distillation is performed in a retort or other vessel which allows the vapour to pass to the condenser almost immediately after its formation. Under these circumstances, the distillate obtained at any period of the operation is almost identical in composition with the vapour that is rising from the liquid, and therefore contains a certain quantity of every constituent of the liquid that produces vapour of sensible tension at the temperature at which ebullition is going on. Hence, in order to effect any great amount of separation in this manner, the distillate must be collected in separate fractions, each of them corresponding to a definite interval of temperature; each fraction must then be fractionally distilled by itself, in the same way as the original liquid, the products which pass over between the same temperatures on the second distillation of the first fractions being collected together; and this process must be repeated as long as any further separation into distinct constituents can be effected. These numerous re-distillations may often be considerably curtailed by using, instead of a retort, a flask fitted with a rather wide branched tube, of the form shown in *fig.* 545. The thermometer is inserted into the upright limb of the branched tube, and is so adjusted in the cork or piece of india-rubber tube which holds it in its place, that the top of the bulb is just below the opening of

Fig. 545.



the side branch by which the vapour passes to the condenser. In an apparatus thus arranged, the vapour rising from the liquid comes in contact with a considerable surface of glass cooled by contact with the air, before it is able to leave the distilling vessel: the consequence is that, in proportion as it rises above the surface of the boiling liquid, it becomes more and more completely freed from its less volatile constituents; and the vapour which ultimately reaches the condenser, at any stage of the operation, is identical with the most volatile portions that would be obtained by the repeated fractional distillation of the liquid resulting from the complete condensation of the vapour existing in the flask at the time. In fact, one distillation made in this way is equivalent to several made in a retort; nevertheless, this method is not always applicable, since the temperature of the boiling liquid requires to be always considerably higher than that of the liquid which is actually distilling, otherwise the whole of the vapour would be condensed before reaching the exit tube—and this would sometimes cause chemical alteration of the substance.

The composition of the distillate which a liquid yields at any period of its distillation does not depend solely upon the tension of the vapours of its several constituents at the temperature of ebullition; it is greatly influenced also by their relative proportions, and by the densities of their vapours. In distilling a volatile liquid containing a small quantity of a less volatile one (for instance, benzene containing a little water), it may very often be noticed that the whole of the less volatile constituent is contained in the first few drops of the distillate. This is because the latter substance produces vapour of whatever tension corresponds to the temperature of ebullition of the mass of the liquid, just as a larger quantity of it would do; this vapour diffuses itself through that of the more volatile constituent and is carried forward with it into the condenser; a further quantity of the less volatile vapour is then formed, and the process continues thus until the whole of the less volatile liquid has been volatilised, although the temperature may not have approached within many degrees of its boiling point.

The influence of the vapour-densities of the several constituents of a mixed liquid, upon the rapidity with which they respectively distil, has been specially pointed out by Wanklyn (Proc. Roy. Soc. xii. 534) and by Berthelot (Compt. rend. lvii. 430). Leaving out of consideration the influence of the adhesion of the ingredients for each other, the quantity of each ingredient which distils may be found by multiplying its tension at the boiling point of the mixture by its vapour-density. Hence, the liquid whose vapour has the highest tension will not necessarily distil the quickest: what the other liquids want in tension, they may make up by the greater density of the vapours which they give off. Wanklyn gives the following experiment in illustration of this effect: 18 grms. of methylic alcohol—boiling point 66°, vapour-density 1·107—was mixed with 17 grms. of iodide of ethyl—boiling point 72°, vapour-density 5·397—and the mixture was distilled until rather more than one-third had passed over. The distillate (14·7 grms.) consisted of 6·0 grms. of methylic alcohol and 8·7 grms. of iodide of ethyl, showing that the less volatile constituent, owing to its greater density of vapour, had distilled most quickly. When the vapour-densities and tensions are inversely proportional, the mixture must distil over unchanged. This influence of vapour-density goes a great way to explain why homologous bodies are so difficult to separate by fractional distillation. The more complex the formula the higher the boiling point, but also the higher the vapour-density, and therefore the greater the value of the vapour. It also explains why oils, &c. distil so readily in steam; for aqueous vapour is one of the lightest, while oily vapours are generally heavy. (Wanklyn, *loc. cit.*)

The action of the sun upon the water at the surface of the earth causes a natural process of distillation upon an enormous scale to be always going on. The water evaporated from the earth's surface rises in the atmosphere as vapour, and being afterwards deprived of its heat of vaporisation—partly by radiation into space, and partly by contact with mountain summits, or with the cold air existing at high elevations—returns to the earth in the various forms of dew, mist, rain, snow, hail, &c. In this way an immense quantity of water is being continually lifted from the sea-level, a large proportion of which does not fall again directly into the sea, but, being deposited on elevated portions of the land, becomes the inexhaustible source whence streams and rivers are supplied. The watery vapour which reaches the higher and colder regions of the atmosphere, is there condensed into snow. This, as it falls again towards the earth, returns to the condition of water, if the air through which it passes is sufficiently warm to liquefy it; but part of it reaches the earth unmelted, and that which falls upon regions whose mean temperature is below zero, accumulates to form the enormous masses of ice known as glaciers. Now it is universally admitted by geologists that, at an epoch by no means (geologically) remote, extensive glaciers existed where none have been known within historic times, and that glaciers which still exist had then a very much greater extent. In order to account for the former existence of so much larger a quantity of ice at the surface of the earth than that which is now to be found, it has often been supposed that, at the period when this occurred, the mean temperature of the earth was considerably lower than at present. But, as Tyndall has pointed out (*Heat considered as a Mode of Motion*, pp. 192, 193), even admitting such to have been the case, the observed result would not have followed. If cold is necessary to condense the vapour of water into ice, heat is no less needed for the first production of the vapour. Hence the condition of the earth which is in reality indicated by the vast development of glaciers in former ages, is one in which the process of distillation went on more rapidly. These considerations have been recently carried further by Frankland. He has shown, by the comparison of well-established data, that the height of the line of perpetual snow above the sea-level at different parts of the earth, depends, not only upon the temperature, but also upon the amount of atmospheric precipitation which takes place; and he concludes, from Tyndall's experiments on the absorption and radiation of heat by aqueous vapour (see RADIATION OF HEAT), that the condensation of the vapour contained in the atmosphere takes place chiefly by the direct radiation of its heat of vaporisation into space. If this conclusion is correct, condensation must have occurred with nearly equal readiness at all stages of the earth's history, and all that was therefore necessary to cause a greater atmospheric precipitation in past times, was a more rapid supply of aqueous vapour. Hence, according to Frankland, the glacial epoch of the geologists is an indication of a higher mean temperature of the earth's surface in former ages, and not of a lower temperature. The climatological conditions of this epoch he considers to have been a necessary consequence of the continuous cooling of the earth's crust from the high temperature which it is admitted to have had at a still earlier era to that which it has at present. In the earlier ages alluded to, the temperature of the earth is supposed to have been such that a great part of the waters of our present ocean must have existed as vapour; and notwithstanding that rapid condensation of this vapour must have occurred, the surface of the earth was too hot to allow the precipitated water to accumulate as ice. But as the cooling progressed, the temperature of the land would fall more quickly than that of the ocean; hence a period would arrive when the former would be so far cooled that ice could accumulate upon it, while the temperature of the water still remained such that evaporation, and consequently condensation, went on much more rapidly than at present. It is during this period that, according to Frankland, the glacial epoch occurred. Its cessation he attributes to the further action of the same cause as that which produced it; namely, to the progressive cooling of the earth, which has now arrived at such a point that evaporation no longer takes place with sufficient rapidity to supply the materials required for the formation of the enormous glaciers of former ages. It is impossible to discuss here the cause of the former high temperature of the earth's surface, indicated by the tropical fauna and flora which preceded the glacial epoch, and, according to Frankland, by the glacial epoch itself; but it has been proved by Thomson that, for ages long anterior to either of the periods referred to, the internal heat of the earth can have produced no sensible effect upon the climate of the surface.

Just as in the process of distillation, as carried on in the laboratory, there is a transference of heat from the retort to the condenser, and consequently a constant tendency to the approximation of their temperatures: so one of the effects of the great natural process of distillation is the partial equalisation of the temperature of different parts of the earth's surface, and of the different strata of the atmosphere.

Various instruments and processes, mostly depending on principles already explained in this article, have been proposed for measuring the quantity of aqueous vapour existing in the air at any given time. A full description of all the most important of them will be found in the article HYGROMETER.

SUBLIMATION.—When, during the distillation of a volatile substance, the temperature of the receiver is kept so low that the vapour which enters it passes at once into the solid state, without previous liquefaction, the process is called sublimation, and the product a sublimate. This process is often resorted to for the purification of substances which volatilise rapidly at temperatures below their melting points.

Changes of Physical Structure.—Some solid substances are capable of existing under two or more forms distinguished from each other by differences of specific gravity, hardness, crystalline form, fusibility, optical and electrical properties, &c. Carbon, for instance, exists as diamond, graphite, and charcoal, as well as in other secondary modifications; phosphorus occurs either as an easily fusible, translucent, yellowish, crystalline substance, or as a much less fusible, opaque, amorphous body of a brick-red colour; and so for many other substances, simple and compound. It thus often happens that the different modifications of the same substance differ more in their physical properties, than other substances do which are chemically distinct; and the passage from one modification to another, though not amounting to a change of state of aggregation, may be considered as a phenomenon of the same class as such changes. Accordingly, it has been found, in all cases in which this point has been investigated, that the passage of a solid body from one modification to another, is attended either with development or with absorption of heat. The experiments which have been made on this subject are not numerous enough to enable any general conclusions to be drawn from them with great certainty, but they appear to indicate that development of heat usually attends the passage from a vitreous or amorphous condition to a crystalline condition, and consequently that the opposite change is accompanied by absorption of heat.

The following are examples of transformations of the kind under consideration:—1. If melted sugar be allowed to cool to about 38°, and then, while it is still soft and viscid, be rapidly and frequently extended and doubled up, till at last it consists of threads, as in drawn sugar, the temperature of the mass quickly rises so as to become insupportable to the hand. After this liberation of heat, the sugar on again cooling, is no longer a glass, but consists of minute crystalline grains and has a pearly lustre. The same change may occur in a gradual manner, as when a clear stick of barley-sugar becomes white and opaque in the atmosphere (**Graham**, *Elements of Chemistry*, 2nd ed. i. 45).—2. When the soft vitreous sulphur, obtained by pouring sulphur melted at 180° or 200° into cold water, is gradually heated in an air-bath of which the temperature is about 98°, the temperature of the sulphur, as soon as it reaches 93°, rises suddenly to 110°, and it then passes immediately into the hard crystalline state which it would have assumed gradually at the ordinary temperature (**Regnault**, Ann. Ch. Phys. [3] i. 205). The prismatic crystals of sulphur obtained by fusion have been long known to pass gradually into octahedral crystals. The same change takes place much more quickly when the crystals are agitated, or when they are put in contact with sulphide of carbon, even if this liquid is already saturated with sulphur. **Mitscherlich** found that the rapid transformation of prismatic into octahedral sulphur which occurs under these circumstances was attended by the evolution of a quantity of heat sufficient to raise the temperature of the sulphur employed by 12°, or which, taking into account the specific heat of sulphur, amounted to 2·27 units of heat per gramme of sulphur (*ibid.* xlvi. 124). **Favre**, who has estimated by an indirect process (Jahresber. 1853, p. 29) the heat evolved in the transformation of one variety of sulphur into another, finds that the quantity of heat liberated, when one equivalent (16 parts) of ordinary sulphur is converted into the modification insoluble in sulphide of carbon, amounts to 3102 units, and that the conversion into the same modification of one equivalent of soft vitreous sulphur, evolves 3804 units of heat.—3. Selenium, when completely melted and then rapidly cooled, constitutes a black mass with a brilliant surface and a fracture exactly resembling that of obsidian or of black glass. When this is heated very gradually, a sudden rise of temperature to 200° or 230° takes place as soon as the thermometer arrives at 96° or 97°. The selenium is afterwards of a bluish grey colour, and has a distinctly metallic lustre. Its fracture, instead of being vitreous, now shows a fine granular structure like that of grey cast iron. The heat evolved in the transformation is estimated by **Regnault** as sufficient to raise the temperature of the selenium operated upon by more than 200 degrees (Ann. Ch. Phys. [3] xlvi. 290).—4. According to **Favre** (*loc. cit.*), 28,246 units of heat are evolved when one equivalent (31 parts) of common phosphorus is converted into red phosphorus.—5. The transformation of 1 grm. of arragonite into calc-spar corresponds to the evolution of 12·9 units of heat (**Favre** and **Silbermann**, Ann. Ch. Phys. [3] xxxvii. 435).—6. Many amorphous minerals and artificially prepared metallic oxides become temporarily incandescent when gently heated, and are then found to have become crystalline without having undergone any alteration in weight. Gadolinite (silicate of yttrium) exhibits this behaviour in a remarkable degree. (For further examples of analogous changes, see **Gmelin's** *Handbook*, i. 104–107.)

The existence of ozone seems to prove that the same chemical substance may exist even in the gaseous state, in more than one modification, and analogy renders it probable that, when such is the case, the transformation of one modification into the other is attended by calorimetric phenomena. Sulphur-vapour at temperatures only slightly above the boiling point of sulphur, and at 800° and upwards, is an instance of another kind of difference in the properties of one and the same gaseous substance, which undoubtedly depends on the quantity of heat present in it, although the heat needed to change the one modification into the other has not been measured.

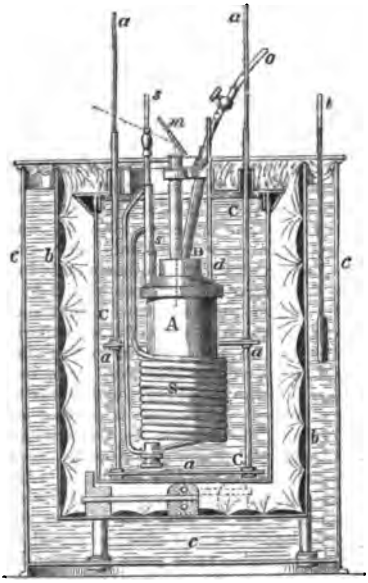
4.—*Relations of Heat to Chemical Affinity.*

Whatever may be the real nature of that property of matter called **chemical affinity**, by virtue of which mutual alterations of composition occur when chemically dissimilar bodies are brought together under appropriate conditions, one most important fact is clearly established with regard to it; namely, that its manifestations are always accompanied by the production or annihilation of heat. Change of composition, or chemical action, and heat are mutually convertible: a given amount of chemical action will give rise to a certain definite amount of heat, which quantity of heat must be directly or indirectly expended, in order to reverse or undo the chemical action that has produced it. The production of heat by chemical action, and the definite quantitative relation between the amount of heat evolved and the quantity of chemical action which takes place, are roughly indicated by the facts of our most familiar experience; thus, for instance, the only practically important method of producing heat artificially consists in changing the elements of wood and coal, together with atmospheric oxygen, into carbonic anhydride and water, and every one knows that the heat which can be thus obtained from a given quantity of coal is limited and is at least approximately always the same.

The accurate measurement of the quantity of heat produced by a given amount of chemical action is a problem of very great difficulty; chiefly because chemical changes very seldom take place alone, but are almost always accompanied by physical changes involving further calorimetric effects, each of which requires to be accurately measured and allowed for, before the effect due to the chemical action can be rightly estimated. Thus the ultimate result comes, in most cases, to be deduced from a great number of independent measurements, each of which is liable to a certain amount of error. It is therefore not surprising that the results of various experiments should differ to a comparatively great extent, and that some uncertainty should still exist as to the exact quantity of heat corresponding to even the simplest cases of chemical action.

Heat evolved in rapid Combustions.—The reactions in which the evolution of heat is most strikingly evident, are of course those which are accompanied by visible incandescence or combustion; and, accordingly, the earliest experiments on the heat of chemical action had reference solely to the heat disengaged in rapid combustions. Lavoisier and Laplace were the first investigators of this subject. Their experiments, made about 1780, consisted in ascertaining the quantity of ice which could be melted by burning in a current of air known weights of the substances examined. In 1814, Count Rumford made experiments of a similar kind by means of a water-calorimeter. His chief object was to ascertain the relative calorific values of the principal combustible substances in actual use as fuel, and from this point of view his results still possess considerable value, although they cannot lay claim to scientific accuracy. In order to counteract the influence of the air and other external objects upon the temperature of his calorimeter, or at least to reduce that influence to a minimum, Rumford began each experiment when the water of the calorimeter was as much colder than the surrounding air, as (he had found by preliminary trials) it would be hotter at the end of the experiment. In this way, the calorimeter gained heat from the air during the first half of each operation, and lost an almost exactly equal quantity during the second half, so that the total effect was almost nothing. This artifice, employed for the first time by Rumford, has been adopted in nearly every subsequent investigation relating to calorimetry. The experiments of Rumford were followed by those of Crawford, Dalton, and Clement Desormes, and more recently by the investigations of Desprets and Dulong. The researches of the last named physicist were left unfinished at his death, but the results obtained appear to have been much more accurate than those of his predecessors. The most exact and comprehensive researches hitherto made into this subject are, however, those of Favre and Silbermann (Ann. Ch. Phys. [3] xxxiv. 357; xxxvi. 5; xxxvii. 406), and Andrews (Phil. Mag. [3] xxxii. 321 and 426).

Fig. 546.



The calorimeter employed by Favre and Silbermann in their experiments on combustion in oxygen gas, and in other actions whereby large quantities of heat were generated, is represented in section in *fig.* 546, the scale of which is one-fifth of that of the actual apparatus. The calorimeter, properly so called, is the cylindrical vessel C C C, made of copper plated externally with silver and brightly polished, and closed by a cover of the same material. This is surrounded by a second vessel, *b b*, also of silvered copper, but having the polished surface inside, the space between C and *b* being filled with swan's down; outside this again is a third vessel, *ccc*, to the bottom of which *b* is firmly connected by screw-bolts. The annular space which separates this vessel from *b* contains water, the temperature of which is indicated by the thermometer *t*, and which serves to neutralise the effect of accidental variations of the temperature of the atmosphere. The chamber in which the combustions take place is made of gilt copper-plate, and is represented by A. When the combustions are to be made in oxygen, the gas, previously purified, enters this chamber by the tube *d*; the products of combustion escape, if gaseous, by the vertical tube *s*, and pass from thence into the serpentine S, where they give up their heat to the water of the calorimeter, and then finally leave the apparatus by the upper part of the tube *s*: when no gaseous products are formed, the extremity of this tube is closed. If the substance to be burned is a gas, it enters the combustion-chamber by a jet connected with the tube *o*; solid bodies are attached to fine platinum-wires, suspended from the cover B, which closes the combustion-chamber; liquids are burned in small capsules, or in lamps with asbestos wicks; charcoal is placed in a sort of sieve, through the openings of which the oxygen has access to it. The progress of the combustion can be watched in the mirror *m* through a window in the tube below composed of a triple disc of glass, alum, and quartz. The temperature of the water in the calorimeter is kept uniform throughout by means of the agitator *aaa*, which is moved by special mechanism. In all cases where it was practicable to do so, Favre and Silbermann deduced the quantity of substance burned from the weight of the products of combustion.

The apparatus employed by Andrews was of much simpler construction. When the substances to be combined were in the gaseous state, and the products of combustion were also gaseous, the two gases were mixed in the proper proportions, as in a eudiometric experiment, and introduced into a vessel of thin sheet copper, of about 24 cubic inches capacity. This vessel was closed by a screw, through which passed a silver wire, insulated from it by a cork, and connected by a thin platinum wire within the vessel to a second silver wire soldered to the screw itself. By passing a voltaic current through the platinum wire for an instant, it could be heated to redness and the gaseous mixture exploded. The copper vessel was introduced into a larger vessel, which was filled up with water: this was suspended in a cylinder provided with a movable cover, and the whole was enclosed in an outer cylindrical vessel, arranged so as to admit of its being made to rotate upon its shorter axis. The apparatus having been mounted, was caused to rotate, so as to bring every part to a uniform initial temperature, which was carefully read off by a very sensitive thermometer. The thermometer was then withdrawn; the gases exploded; the outer vessel of water closed by a cork; and the apparatus caused to rotate for thirty-five seconds. The thermometer was then again introduced and the rise of temperature ascertained; after which the apparatus was made to rotate a third time for thirty-five seconds, and the temperature again observed, in order to ascertain the cooling effect of the atmosphere upon the apparatus during the time that the experiment lasted: it was found that this effect seldom exceeded $\frac{1}{400}$ of the total quantity to be measured.

When solid bodies were burned in oxygen, the combustion was effected in a copper vessel, of about 250 cubic inches in capacity, which was filled with oxygen; a known weight of the combustible was placed in a small platinum dish, and when all was ready, it was fired by means of a voltaic current sent through a very fine platinum wire. The vessel in which the combustions took place was immersed in a large cylinder containing a known quantity of water, and surrounded by an outer vessel of tin-plate, to prevent radiation. The copper vessel could be moved up and down in the water by means of a lever. Particular expedients were sometimes required to insure ignition: thus, in burning zinc-filings and other metals in oxygen, a small fragment of phosphorus (from 1 to 8 milligrammes) was employed to kindle the metal; the weight of the phosphorus being known, the heat evolved by it could be calculated and deducted from the total amount produced. Some of these experiments lasted a quarter of an hour and upwards, so that the correction for the cooling effect of the air became of considerable importance.

When the combustions were made in chlorine, the substance to be burned was enclosed in a thin glass bulb, which was broken by agitation after being immersed in the gas; in these experiments it was not necessary to apply heat to cause the combustion to begin. The chlorine itself was usually contained in a glass vessel, filled with it by displacement; in the experiments on potassium, a brass vessel was used, perfectly dry chlorine having no action on brass. An excess of the metal was always used, so as to insure the complete absorption of the chlorine, and the quantity of the latter substance consumed was, in most cases, ascertained by weighing the quantity of water which rushed into the vessel after the experiment on opening it under water.

The following table gives the quantities of heat, expressed in heat-units (gramme-degrees), evolved in the combustion of various elementary substances in oxygen, referred (1) to 1 grm. of each element burned, (2) to 1 grm. of oxygen consumed, (3) to 1 atom (expressed in grms.) of the several elements.

Heat of Combustion of Elementary Substances in Oxygen.

Substance.	Product.	Units of heat evolved			Observer.
		by 1 grm. of substance.	by 1 grm. of oxygen.	by 1 at. of substance.	
Hydrogen . .	H^2O	33881 34462	4235 4308	33881 34462	Andrews. Favre & Silbermann.
Carbon:					
Wood-charcoal .	CO^2	7900 8080	2962 3030	94800 96960	Andrews. Favre & Silbermann.
Gas-retort carbon	„	8047	3018	96564	„
Native graphite .	„	7797	2924	93564	„
Artificial graphite	„	7762	2911	93144	„
Diamond . .	„	7770	2914	93940	„
Sulphur:					
Native . .	SO^2	2220	2220	71040	„
Recently melted .	„	2260	2260	72320	„
Flowers . .	„	2307	2307	73821	Andrews.
Phosphorus:					
(yellow) . .	P^2O^5	5747	4454	178157	„
Zinc . . .	ZnO	1330	5390	86450	„
Iron . . .	Fe^3O^4	1582	4153	88592	„
Tin . . .	SnO^2	1147	4230	135360	„
Copper . . .	CuO	603	2394	38304	„

NOTE.—Andrews' determinations have been recalculated from the original experimental numbers, using the atomic weights and specific gravities of gases adopted in this Dictionary, and therefore the numbers in the above table do not always agree precisely with those contained in the general table of results which he has himself given (Phil. Mag. [3] xxxii. 432).

The following results have been obtained by the complete combustion of partially oxidised substances:

Substance.	Product.	Units of heat evolved		Observer.
		by 1 grm. of substance.	in formation of 1 molecule of the ultimate product.	
Carbonic oxide .	CO^2	2403 2431	67284 68064	Favre & Silbermann. Andrews.
Stannous oxide .	SnO^2	519	69584	„
Cuprous oxide .	CuO	256	18304	„

The substances enumerated in this table contain exactly half as much oxygen as the completely oxidised products, and on comparing the amount of heat evolved in the formation of one molecule of stannic or cupric oxide from the corresponding lower oxide, with the quantity produced when a molecule of the same product is formed by the complete oxidation of the metal in one operation (see previous table), we find that the combination of the second half of the oxygen contained in these bodies evolves sensibly half as much as the combination of the whole quantity. In the formation of carbonic anhydride, however, the second half of the oxygen appears to develope more than two-thirds of the total amount of heat; but this result is probably due, in part at least, to the fact that when carbon is burned into carbonic anhydride, a considerable but unknown quantity of heat is expended in converting the solid carbon into gas, and thus escapes measurement; while, in carbonic oxide, the carbon already exists in the gaseous form, and therefore no portion of the heat evolved in the combustion of this substance, is similarly expended in producing a change of state.

It seems probable also, that a similar explanation may be given of the inequalities in the quantities of heat produced by the combustion of different varieties of pure carbon and of sulphur,—that is to say, that a portion of the heat generated by the combustion of diamond and graphite goes to assimilate their molecular condition to that of wood-charcoal, and that there is an analogous expenditure of heat in the combustion of native sulphur: indeed, with regard to the latter case, it is proved by direct experiments (see p. 102), that the opposite change to that supposed to take place here of recently melted sulphur into the same molecular condition as native sulphur is accompanied by disengagement of heat.

In like manner, the heat evolved in combustions may in some cases be in excess of that due to the strictly chemical action which takes place: thus, when the product of combustion is solid, part of the heat must be ascribed to the solidification of the oxygen absorbed. Again, the heat of combustion of hydrogen, as given above, includes the latent heat of vaporisation of the water formed. In Andrews' experiments the temperature of the calorimeter was about 20° C.: at this temperature the latent heat of vaporisation of 9 grms. of water (the quantity formed from 1 grm. or atom of hydrogen) may be taken as = 5500; and deducting this quantity from 33,881, we have 28,381 as the number of units of heat evolved by the chemical combination of 1 grm. hydrogen and 8 grms. oxygen, according to these experiments. Favre and Silbermann do not give the temperature of their calorimeter, but probably the same correction may be applied to their experiments without much error: they then give 34,462—5500 = 28,962 as the true heat of combustion of 1 grm. of hydrogen.

The experiments which have been made on the heat of combustion of definite compounds, other than the three already mentioned, relate almost exclusively to bodies composed of carbon and hydrogen, or of carbon, hydrogen, and oxygen. The results obtained by Favre and Silbermann and Andrews are contained in the following table. The numbers here given represent the total heat produced, and therefore include that due to the condensation of the vapour of water formed in the experiments.

Many of these numbers must be regarded as approximations only (and sometimes as not very close approximations) to the truth. The chief causes of uncertainty with regard to them, besides the difficulties inherent in the experimental determinations themselves, are the different calorimetric properties of the substances examined—differences, that is, in regard to specific and latent heats—and, in some cases, their admittedly doubtful purity. Hence it is impossible to trace any exact correspondence between the composition of the bodies experimented upon, and the amount of heat which they evolve upon combustion. A few general conclusions are, however, indicated with sufficient clearness to make it worth while to dwell upon them briefly.

In the first place it appears that the heat of combustion of a compound is in general less than the heat of combustion of its elements. This rule is verified in the case of all the hydrocarbons given in the table, with the exception of olefiant gas, whose heat of combustion is almost exactly the same as that of its constituents, according to Favre and Silbermann's determinations, and somewhat greater, according to Andrews. When a hydrocarbon is burned into carbonic anhydride and water, the chemical change which takes place consists, not merely in the union of carbon and hydrogen with oxygen, but also in their separation from their previous state of combination with each other. Now, it is an almost self-evident proposition, and one which has moreover received direct experimental confirmation, that whatever may be the calorimetric effect of any given chemical change, the calorimetric effect of its reversal is equal and opposite. Hence, if we suppose the combination of carbon and hydrogen—to form marsh-gas, for example—to be accompanied by evolution of heat, we must suppose that their separation is attended by the disappearance of an equal quantity of heat. The heat produced by the combustion of one molecule of marsh-gas, CH^4, is therefore less than the quantity due to the combustion of one atom of (gaseous) carbon and four atoms of hydrogen, by the quantity of heat absorbed when these atoms separate from combination with each other. Assuming (for want of more certain data) that the heat of combustion of an atom of gaseous carbon is twice that of a molecule of carbonic oxide, we have, for the heat of combustion of $C + H^4$ (in round numbers), $134{,}600 + (4 \times 34{,}460) = 272{,}440$; but the heat of combustion of CH^4 is 209,000, which gives $272{,}440 - 209{,}000 = 63{,}440$ as the number of units of heat produced by the combination of 1 atom of carbon with 4 atoms of hydrogen, or absorbed when these atoms separate. In like manner, we have, for the heat of combustion of $C^2 + H^4$, $(2 \times 134{,}600) + (4 \times 34{,}460) = 407{,}040$ units; and deducting from this the heat of combustion of olefiant gas, we have $407{,}000 - 332{,}000 = 75{,}000$ for the calorimetric effect due to the separation of the atoms of a molecule of olefiant gas from each other. The difference between 63,400 (the heat of formation of CH^4) and 75,000 (the heat of formation of C^2H^4), namely 11,600, may perhaps be taken as representing the calorimetric effect of the combination or separation of the two atoms of carbon contained in olefiant gas. The fact that the heat of combustion of olefiant gas, as found by direct experiment, is very nearly equal to the sum of the heats of its constituents, when the heat of an atom of carbon is taken at 96,960 units, the quantity deduced from the combustion of wood-charcoal, probably indicates that the heat of vaporisation required to change the physical condition of two atoms of carbon from that of wood-charcoal to that which it has in the form of olefiant gas, is nearly the same as the heat required to separate the atoms of a molecule of olefiant gas from each other. That the heat of vaporisation of carbon is very considerable is further indicated by the great difference, already alluded to, between the calorific effect of the first and second atoms of oxygen contained in carbonic anhydride, *Heat of Combustion of Compounds in Oxygen.*

Substance.	Formula.	Molecular weight.	Units of heat evolved.		Observer.
			by 1 grm. of substance.	by 1 molecule of substance.	
Marsh-gas . . .	CH^4	16	13108	209728	Andrews.
			13063	209008	Favre and Silbermann.
Olefiant gas . . .	C^2H^4	28	11942	334376	Andrews.
			11858	332024	Favre and Silbermann.
Amylene . . .	C^5H^{10}	70	11491	804370	"
Paramylene . . .	$C^{10}H^{20}$	140	11303	1582420	"
Hydrocarbon: (from amylic alcohol boiling point 180°)	$C^{11}H^{22}$	154	11262	1734348	"
Cetylene . . .	$C^{16}H^{32}$	224	11055	2476328	"
Metamylene . . .	$C^{20}H^{40}$	280	10928	3059840	"
Oil of lemons . . .	$C^{10}H^{16}$	136	10959	1490424	"
Oil of turpentine . .	$C^{10}H^{16}$	136	10852	1475872	"
Terebene . . .	$C^{10}H^{16}$	136	10662	1450032	"
Ether	$C^4H^{10}O$	74	9028	668072	"
Amylic ether (impure ?) .	$C^{10}H^{22}O$	158	10188	1609704	"
Methylic alcohol . .	CH^4O	32	5307	169824	"
Ethylic alcohol . .	C^2H^6O	46	7184	330464	"
			6850	315100	Andrews.
Amylic alcohol . .	$C^5H^{12}O$	88	8959	788392	Favre and Silbermann.
Cetylic alcohol: (latent heat of fusion added) . .	$C^{16}H^{34}O$	242	10629	2572218	"
Formic acid . . .	CH^2O^2	46	2091	96186	"
Acetic acid . . .	$C^2H^4O^2$	60	3505	210300	"
Butyric acid . . .	$C^4H^8O^2$	88	5647	496936	"
Valeric acid . . .	$C^5H^{10}O^2$	102	6439	656778	"
Palmitic acid . . .	$C^{16}H^{32}O^2$	256	9316	2384896	"
Stearic acid . . .	$C^{18}H^{36}O^2$	284	9716	2759344	"
Formate of methyl . .	$C^2H^4O^2$	60	4197	251820	"
Acetate of methyl . .	$C^3H^6O^2$	74	5342	395308	"
Formate of ethyl . .	$C^3H^6O^2$	74	5279	390646	"
Acetate of ethyl . .	$C^4H^8O^2$	88	6293	553784	"
Butyrate of methyl .	$C^5H^{10}O^2$	102	6798	693447	"
Butyrate of ethyl . .	$C^6H^{12}O^2$	116	7091	822556	"
Valerate of methyl . .	$C^6H^{12}O^2$	116	7376	855616	"
Valerate of ethyl . .	$C^7H^{14}O^2$	130	7835	1018550	"
Acetate of amyl . .	$C^7H^{14}O^2$	130	7971	1036230	"
Valerate of amyl . .	$C^{10}H^{20}O^2$	172	8544	1469568	"
Palmitate of cetyl (spermaceti) .	$C^{32}H^{64}O^2$	480	10342	4964160	"
Hydrate of phenyl . .	C^6H^6O	94	7842	737148	"
Sulphide of carbon . .	CS^2	76	3400	258400	"

as well as by the fact that the heat of combustion of a molecule of sulphide of carbon exceeds the sum of the heats of its constituents.

It will be understood that the foregoing calculations are given, rather for the sake of drawing attention to the necessity of taking account of *all* the changes, whether chemical or physical, which accompany a given chemical reaction, when we are discussing the quantity of heat produced by it, than because the results arrived at are supposed to be numerically accurate. Indeed it is by no means probable that these results are, at best, anything more than roughly approximative; for, to mention no other source of uncertainty, the assumption that we have made, that the heat produced by the complete combustion of carbon is twice as great as that evolved by the combustion of the same quantity of carbon in the form of carbonic oxide, is most likely not strictly true. For it has been pointed out by **Butlerow** that the four units of combining capacity (CLASSIFICATION, i. 1010 *et seq.*) possessed by one atom of carbon are not exactly equivalent to each other in chemical function, and **Erlenmeyer** has suggested, with great probability, that the difference between them is due to differences in the strength of the chemical affinity with which each unit enters into combination (see references in the article FORMULÆ, ii. 704). If this be so, the combination of an atom of carbon with one atom of oxygen must evolve more heat than the combination of the product so formed (carbonic oxide) with a second atom of oxygen.

The numbers in the above table show that the heat evolved by the combustion of equal weights of the hydrocarbons $(CH^2)^n$, homologous with olefiant gas, diminishes as their molecular weights increase. But it is not easy to say how far this result may be due to accidental causes (the numbers given are deduced from a single experiment, except in the case of olefiant gas, for which Favre and Silbermann obtained very concordant results in two experiments), or to the influence of the physical properties of the substances. It may be remarked that the isomeric substances, oil of lemons, oil of turpentine, and terebene, also gave different quantities of heat, although their molecular weights are the same.*

The acids homologous with acetic acid may be regarded, empirically, as formed by the combination of the hydrocarbons $(CH^2)^n$ with oxygen; that is, they may be considered as products of the partial combustion of the hydrocarbons. Hence, we should expect each acid to give out, when burned, less heat than the hydrocarbon containing the same quantity of carbon and hydrogen, and this is shown by the numbers in the above table, to be really the case, the difference between the heat of combustion of an acid and that of a given hydrocarbon being greater in proportion as the acid is more oxidised. Thus, starting from amylene, C^5H^{10}, and comparing with it quantities of valeric, butyric, and acetic acids which contain the same quantity of carbon and hydrogen, we have the following numbers:

1	molecule	amylene,	C^5H^{10}	$= 70$	produces	804400	units of heat.
1	„	valeric acid,	$C^5H^{10}O^2 = C^5H^{10} + O^2$	$= 102$,	„	656800	„
$1\frac{1}{4}$	„	butyric acid,	$1\frac{1}{4}C^4H^8O^2 = C^5H^{10} + O^{2\frac{1}{2}}$	$= 110$,	„	621200	„
$2\frac{1}{2}$	„	acetic acid,	$2\frac{1}{2}C^2H^4O^2 = C^5H^{10} + O^5$	$= 150$,	„	525750	„

Compared in this way, the difference in composition between amylene and valeric acid, namely O^2, is four times as great as that between valeric acid and butyric acid, and the corresponding differences in the heats of combustion of these substances are exactly almost in the same proportion: but this close agreement is, probably, in great part accidental: for the heat of combustion of acetic acid is decidedly greater than what might be calculated in the same way.

The table further shows that isomeric substances by no means always give out equal quantities of heat when burned. For instance, acetic acid, $C^2H^4O^2$, produces considerably less heat than its isomer, formate of methyl; butyric acid, $C^4H^8O^2$, less than its isomer, acetate of ethyl; valeric acid, $C^5H^{10}O^2$, less than its isomer, butyrate of methyl. That differences of this kind would be found to exist, might have been deduced, with considerable probability, from the differences in the chemical constitution of the acids and of the isomeric ethers: for, of the four equivalents of oxygen contained in these compounds, one must be regarded as combined with hydrogen, and the other three with carbon in the acids; whereas, in the ethers, all four equivalents of oxygen are combined with carbon. Hence, the differences between the heats of combustion of the acids $C^nH^{2n}O^2$ and those of the isomeric ethers may be ascribed, at least in part, to the difference between the heat of combustion of an equivalent of carbon and that of an equivalent of hydrogen; but considerations, such as have been already alluded to, make it impossible to assign any exact numerical value to this difference.

But, according to the experiments hitherto made, not only do the acids differ from the isomeric ethers, in the quantity of heat which they produce when burned, but the ethers differ from each other: for instance, acetate of methyl produces more heat than its isomer formate of ethyl; valerate of methyl, more than its isomer butyrate of ethyl; acetate of amyl, more than its isomer valerate of ethyl. It is not easy to suggest any chemical reason for the existence of such differences as these; nor even to discover any empirical relations of a general kind among the experimental results.

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* Favre and Silbermann assign to oil of lemons half the molecular weight of oil of turpentine, but without giving any reason for so doing.

[For the methods of calculating the heating powers of different kinds of fuel, and the temperature produced by its combustion, for practical purposes, see the article FUEL, ii. 722 *et seq.*]

Combustions in Chlorine, and direct combination of Chlorine, Bromine, and Iodine.—The following table gives the quantities of heat evolved by the direct union of various elements with gaseous chlorine:

Substance.	Product.	Units of heat evolved			Observer.
		by 1 grm. of substance.	by 1 grm. of chlorine.	by 1 at. (=35·5 grms.) of chlorine.	
Hydrogen .	HCl	24087	678	24087	Abria.
		23783	670	23783	Favre and Silbermann.
Phosphorus .	PCl^5(?)	3422(?)	607	21548	Andrews.
Potassium .	KCl	2655	2943	104476	"
Iron . .	Fe^2Cl^3	1745	921	32695	"
Zinc . .	ZnCl	1529	1427	50658	"
Tin . .	$SnCl^4$	1079	897	31722	"
Arsenic .	$AsCl^3$	994	704	24992	"
Copper . .	CuCl	961	859	30494	"
Antimony .	$SbCl^3$	707	860	30491	"
Mercury .	?	?	822	29181	"

The heat evolved by the direct union of bromine and iodine with zinc and iron has also been determined by **Andrews** (Trans. Roy. Irish Acad. xix. quoted in **Miller's** *Chemical Physics*, p. 341): the results obtained are given in the next table:

Metal.	Product.	Units of heat evolved		
		by 1 grm. of metal.	by 1 grm. of bromine or iodine.	by 1 at. of bromine or iodine.
		Bromine.		
Zinc . .	ZnBr	1269	508	40640
Iron . .	Fe^2Br^3	1277	298	23833
		Iodine.		
Zinc . .	ZnI	819	209	26617
Iron . .	Fe^2I^3	463	63	8046

Heat produced by reactions in the Wet Way.—Of the various reactions in the wet way, which have been studied calorimetrically, it will be most convenient to consider first those which take place between water and other bodies, since such actions intervene in many other cases also.

Dilution of Acids with Water.—The heat produced by the dilution of strong acids, especially sulphuric acid, has been the subject of many investigations, the most accurate of which are probably those of **Favre** and **Silbermann**, **Thomsen** (Pogg. Ann. lxxxviii. 349; xc. 261; Jahresber. 1853, p. 30); and **Favre** and **Quaillard** (Compt. rend. l. 1150). We give below a few of the results obtained.

Sulphuric acid, $SO^4H^2 = 98$.

Thomsen determined the quantity of heat evolved by the mixture of strong sulphuric acid, and of the same previously diluted with different quantities of water, with an excess of water—that is, with so much that any further quantity did not increase the amount of heat evolved. He found that the addition of an excess of water

to 98 grms. (=1 molecule)	SO^4H^2	evolved	17,248	units of heats.
to 116 "	$SO^4H^2.H^2O$	"	10,848	"
to 152 "	$SO^4H^2.3H^2O$	"	6288	"
to 188 "	$SO^4H^2.5H^2O$	"	4480	"

Favre has determined, in conjunction with Silbermann and with Quaillard, the quantity of heat produced by the successive additions of known quantities of water to strong sulphuric acid. Both sets of experiments were made with the mercurial calorimeter already described, and represented in *fig.* 531, p. 28. We give here the results published by Favre and Quaillard as being the most recent.

Addition of Water to 98 *grammes* (1 *molecule*) *of Sulphuric Acid.*

Quantities of water added successively. Molecules.	Heat evolved on each successive addition of water.		Total quantity of water added. Molecules.	Total Heat evolved.	Quantities of water added successively. Molecules.	Heat evolved on each successive addition of water.	Total quantity of water added. Molecules.	Total Heat evolved.
⅛	946·68	6375·88			1	885·30	5	13661·90
⅛	885·92				1	754·48	6	14416·38
¼	1711·08				1	591·84	7	15008·22
½	2832·20				1	465·36	8	15473·58
1	. . .	6512·80	1	6512·80	4	1063·66	12	16537·24
½	1842·40	3180·50			4	483·02	16	17020·26
½	1338·10				4	222·46	20	17242·72
1	. . .	3244·00	2	9756·80	4	141·58	24	17384·30
½	1009·40	1814·52			4	86·96	28	17471·26
½	805·12				4	65·06	32	17536·32
1	. . .	1840·80	3	11597·60	4	43·28	36	17579·60
1	. . .	1179·00	4	12776·60	4	32·08	40	17611·68

A little heat was still produced by the addition of the sixtieth molecule of water.

These numbers show that a given quantity of water added to sulphuric acid evolves the same quantity of heat, whether it be added all at once, or in successive small portions, and that the heat which a given quantity of water produces is, accordingly, less in proportion as the amount previously added is greater.

Nitric Acid, $NO^3H = 63$.

The following table gives the results of Thomsen's experiments on the heat evolved on adding an excess of water to nitric acid, either undiluted or already containing a certain quantity of water. The numbers refer, as usual, to molecular proportions of acid and water expressed in grammes:—

NO^3H mixed with excess of water evolved 7560 units of heat.
$(NO^3H + 0{\cdot}421\ H^2O)$ mixed with excess of water evolved 5680 ,, ,,
$(NO^3H + H^2O)$,, ,, ,, ,, 4088 ,, ,,
$(NO^3H + 1{\cdot}5\ H^2O)$,, ,, ,, ,, 3760 ,, ,,
$(NO^3H + 1{\cdot}59\ H^2O)$,, ,, ,, ,, 3464 ,, ,,
$(NO^3H + 2\ H^2O)$,, ,, ,, ,, 2712 ,, ,,
$(NO^3H + 2{\cdot}5\ H^2O)$,, ,, ,, ,, 2184 ,, ,,
$(NO^3H + 3{\cdot}5\ H^2O)$,, ,, ,, ,, 1392 ,, ,,
$(NO^3H + 4{\cdot}5\ H^2O)$,, ,, ,, ,, 952 ,, ,,

It will be observed that the heat which can be obtained by the addition of water to nitric acid diminishes as the quantity of water already present in the acid is greater, but that the diminution takes place, at first, much less rapidly than in the case of sulphuric acid.

Acetic Acid, $C^2H^4O^2 = 60$.

The following results are those of Favre and Quaillard: we give them in order to call attention to the absorption of heat (indicated by the *minus* sign in the second column) produced by the first quantities of water added:

Quantities of water added successively.	Heat evolved on each addition of water.		Total quantity of water added.	Quantities of water added successively.	Heat evolved on each addition of water.	Total quantity of water added.
⅛ H^2O	− 72·22	− 135·00		½ H^2O	+ 3·51	2 H^2O
⅛ ,,	− 33·13			½ ,,	5·97	2½ ,,
⅛ ,,	− 17·66			½ ,,	11·28	3 ,,
⅛ ,,	− 11·99			1 ,,	23·45	4 ,,
½ ,,	. .	− 135·16	½ H^2O	1 ,,	27·47	5 ,,
¼ ,,	− 16·65	− 24·87		2½ ,,	82·47	7½ ,,
¼ ,,	− 8·22			2½ ,,	54·73	10 ,,
½ ,,	. .	− 25·18	H^2O	5 ,,	87·72	15 ,,
½ ,,	. .	− 3·56	1½ H^2O	5 ,,	40·54	20 ,,

These numbers plainly show the simultaneous occurrence of two distinct actions—one of them attended with absorption of heat, the other with its production. The former action prevails at first, but gradually diminishes as more and more water is added, until, on the addition of the fourth half-molecule, its effect becomes less than that of the second, and a small evolution of heat takes place. From this point, until between five and seven-and-a-half molecules of water have been added, the calorific effect of a given quantity of water continually *increases* (contrary to what takes place with sulphuric and nitric acids), showing that the heat-absorbing action still takes place, but to a less and less extent, until more than five molecules of water have been added to each molecule of acetic acid.

When successive quantities of alcohol, up to ten molecules, are added to acetic acid, each addition causes absorption of heat; but the numerical results clearly indicate, in this case also, the simultaneous occurrence of distinct phenomena. Favre obtained the following results:

Molecules of alcohol successively added to 1 molecule of acetic acid	1	1	1	1	2	2	2
Units of heat *absorbed* on the addition of each successive quantity	91·91	0·91	7·35	14·88	31·85	41·47	64·50

Absorption of heat also frequently occurs on the dilution of saline solutions, a phenomenon with regard to which numerous quantitative determinations have been made by Favre. It is probable that in these cases, a change takes place more or less analogous to the liquefaction of a solid by solution: acetic acid, or a salt dissolved in a small quantity of water, may be conceived of as being imperfectly liquefied, so that further liquefaction, accompanied by the disappearance of a certain quantity of heat, takes place on the addition of more water. Viewed in this way, these phenomena appear to be comparable with the gradual melting, which, as we have seen (pp. 74 and 76), takes place in some solids under the direct action of heat.

Reaction of Acids and Bases in presence of water.—It will be easily understood that the thermal effects which may result from the reaction of different substances upon each other in presence of water, are even more complicated than any of those which have yet been considered, and therefore that the calorimetric study of these reactions is subject to still more numerous causes of error than that of the foregoing processes. In addition to the different specific heats of the reagents and products, and to the different quantities of heat absorbed by them in dissolving, or given out by them in combining with water, the conversion of soluble substances into insoluble ones, as a consequence of the chemical action, or the inverse change of insoluble into soluble bodies, are among the secondary causes to which part of the calorimetric effect may be due in these cases. The greater number of these disturbing causes may be got rid of, or at least very much reduced in amount, by effecting the reactions in the presence of comparatively large quantities of water, but then the difficulty of accurately measuring the total quantity of heat produced becomes greater.

The following table gives the number of units of heat evolved, according to Favre and Silbermann's experiments, in the transformation of equivalent quantities of various

Oxide of	Equivalents.	Units of Heat evolved with Various Acids:			
		Sulphuric.	Nitric.	Hydrochloric.	Acetic.
Potassium .	47	16083	15510	15656	13978
Sodium . .	31	15810	15283	15128	13600
Ammonium .	26	14690	13676	13536	12649
Barium . .	76·5	. .	15360	15306	13262
Calcium . .	28	. .	16943	16982	14675
Magnesium .	20	14440	12840	13220	12270
Manganese .	35·5	12075	10850	11235	9982
Zinc . . .	40·5	10455	8323	8307	7720
Cadmium . .	64	10240	8116	8109	7546
Copper . .	39·7	7720	6400	6416	5264
Nickel . .	37·7	11932	10450	10412	9245
Cobalt . .	37·7	11780	9956	10374	9272
Lead. . .	111·7	. .	9240	. .	7168
Silver . .	116	. .	6206		

metallic protoxides into neutral salts, the reaction taking place in all cases in presence of a large quantity of water, and the products being all soluble:

The heat evolved by equivalent quantities of potash and soda respectively, in forming neutral salts with the following additional acids, is shown in the next table:

Acids.	Potash.	Soda.	Acids.	Potash.	Soda.
Hydrobromic acid .	15510	15159	Valeric acid . .	. .	13500
Hydriodic acid .	15698	15097	Citric acid . .	13658	13178
Metaphosphoric acid . .	16168	15407	Oxalic acid . .	14156	13752
			Tartaric acid . .	13425	12651
Pyrophosphoric acid	16920	15655	Carbonic acid .	12878	. .
Phosphoric acid .	17766	. .	Hydrosulphuric acid . .	6477	6550
Formic acid . .	. .	13308			

Numerous determinations of a similar kind have also been made by **Andrews** (Trans. Roy. Irish Academy, xix.; Rep. Brit. Associat. 1849, p. 69; see also **Miller's** *Chemical Physics*, p. 352). The following is the most important of the conclusions at which he arrived:—"An equivalent of the same base, combined with different acids, produces *nearly* the same quantity of heat; but an equivalent of the same acid combined with different bases, produces different amounts of heat." It is, however, scarcely needful to point out, that such a difference as is here implied between the chemical behaviour of acids and bases does not really exist in nature, and that its appearing to be indicated by the experiments in question, could only result from the accident of the bases examined representing a greater range of varying chemical energy than the acids.

The results obtained on bringing together an alkali and an acid in various proportions are of considerable interest. They show clearly that, at least in the case of the most distinctly characterised acids, chemical action takes place only between definite atomic proportions of acid and alkali. The numbers given below represent the number of units of heat evolved by one equivalent of potash or soda (the quantity containing 39 pts. potassium, or 23 pts. sodium) when acted on by varying quantities of acid.

1 equivalent potash
with 1 equivalent sulphuric acid gave 15609 units of heat.
„ 2 „ „ „ „ 15609 „ „
„ 1 „ acetic „ „ 13935 „ „
„ 2 „ „ „ „ 13823 „ „ (Favre and Silbermann).

The results of Thomsen's experiments (Jahresber. 1854, p. 30) with sulphuric acid and potash and soda are as follows:

Equivalents of acid		$\frac{1}{3}$	$\frac{2}{3}$	1	$\frac{3}{2}$	2	4
Heat evolved	Soda	5424	10656	15368	15320	15524	15216
	Potash	4968	9880	15368	. .	15248	

It will be seen that the evolution of heat increases sensibly in the same proportion as the quantity of acid used, up to one equivalent, but that beyond this point no further increase in the amount of heat evolved accompanies the augmentation of the quantity of acid. Hence it appears that acid sulphates of potassium and sodium are not formed in presence of a large quantity of water, a conclusion which agrees with Favre and Silbermann's observation, that the evolution of heat which takes place on adding one equivalent of base to a dilute solution of acid sulphate or sulphite of potassium, is the same as if the second equivalent of acid contained in the salt were employed in the free state. By experiments on the heat evolved on adding successive quantities of other acids—such as boric, silicic, phosphoric—to one equivalent of soda or potash, Thomsen found that the heat produced was at first nearly in proportion to the quantity of acid added, but that, as the latter was increased, the evolution of heat increased also, though in a continually slower ratio.

Evolution of Heat in the formation of Aqueous Solutions.—When a gas dissolves in water, the heat due to the chemical action is augmented by that due to the physical phenomenon of the liquefaction of the gas; so also, when a solid body is dissolved in water, the total thermal effect observed is due in part to the chemical action taking place between the water and the solid, and in part to the liquefaction of the substance dissolved. In the former case, the chemical and physical parts of the phenomenon both cause evolution of heat: in the latter case, the physical change occasions disappearance of heat; and if this effect is greater than that due to the chemical action, the ultimate result of the combined process is the production of cold, and it is this which is most usually observed. The following tables contain the results of Favre and Silbermann's experiments, calculated for one gramme of gas or solid salt dissolved.

Solution of Gases in Water.

Name of Gas.	Units of heat evolved.	Name of Gas.	Units of heat evolved.
Hydrochloric acid	449·6	Sulphurous acid	120·4
Hydrobromic acid	235·6	Ammonia	514·3
Hydriodic acid	147·7		

Solution of Salts in Water.

Name of Salt.	Units of heat absorbed.	Name of Salt.	Units of heat absorbed.
Sulphate of potassium	35·3	Nitrate of sodium	45·5
„ sodium	49·1	„ ammonium	65·9
„ ammonium	11·1	„ calcium	27·1
„ calcium	24·7	„ strontium	41·2
„ barium	64·4	„ lead	14·9
„ zinc	14·8	„ silver	31·1
Ferrous sulphate	12·1	Phosphate of sodium	52·3
Uranic sulphate	+10·7	Pyrophosphate of sodium	21·9
Potassio-ferrous sulphate	21·5	Oxalic acid	67·0
Sulphate of aluminium and potassium	23·1	Oxalate of potassium	39·7
Sulphate of aluminium and ammonium	19·0	Acid oxalate of potassium	62·1
Acid sulphate of potassium	25·6	Tartrate of potassium	17·3
Chloride of potassium	51·9	„ sodium	25·2
„ sodium	8·9	Tartaric acid	19·8
„ ammonium	65·1	Tartrate of potassium and sodium	40·9
„ calcium	15·5	Acetate of sodium	28·1
„ barium	16·9	„ calcium	3·5
„ strontium	24·9	„ lead	14·8
„ zinc (anhydrous)	+92·2	Acid acetate of potassium	19·3
Ferrous chloride (anhydrous)	+58·3	Carbonate of sodium	52·7
Cupric chloride (anhydrous)	+73·7	Acid carbonate of potassium	51·5
Bromide of potassium	37·8	Sulphide of potassium (anhydrous)	+96·9
Iodide of potassium	29·2		
Nitrate of potassium	70·5		

NOTE.—The sign *plus* (+) denotes evolution of heat.

The foregoing table includes numbers relating to the solubility of some salts which are, in reality, either quite insoluble or very slightly soluble in water. These numbers are deduced from a comparison of those which represent the heat of formation of these salts with the numbers expressing the heat evolved by the same bases with other acids. The heat of formation of salts which are insoluble, and therefore separate out in the solid form, is usually considerably greater than the heat of formation of soluble salts of the same bases and acids, and it is this excess which in the above table is given as the heat absorbed on solution by such salts as sulphate of barium, sulphate of strontium, &c.

Cold produced by Chemical Decomposition.—The proposition that the thermal effect of the reversal of a given chemical action is equal and opposite to the thermal effect of that action itself, has already been referred to (p. 106) as one which might with great probability be assumed as true. A direct consequence of this proposition is that *the separation of any two bodies is attended with the absorption of a quantity of heat equal to that which is evolved in their combination.* The truth of this deduction has been experimentally established in various cases by Woods (Phil. Mag. [4] ii. 368; iv. 370); Joule (*ibid.* iii. 481) and Favre and Silbermann, by comparing the heat evolved in the electrolysis of dilute sulphuric acid, or solutions of metallic salts, with that which is developed in a thin metallic wire by a current of the same strength; and by comparison of the heat evolved in processes of combination accompanied by simultaneous decompositions, with that evolved when the same combination occurs between free elements.

In the experiments of Woods, a voltaic current was first made to pass through a vessel containing dilute sulphuric acid, and the quantity of gas evolved in a given time was determined, and also the simultaneous rise of temperature, the strength of the current being measured at the same time by the tangent-compass (ii. 460). The electrolytic cell was then removed, and a thin platinum wire introduced between the poles, of such a length as to produce a resistance equal to that of the electrolyte. The quantity of heat evolved in this wire was then determined, and found to exceed that which was previously evolved in the electrolytic cell, by a quantity equal to that which would be evolved by the combination of the oxygen and hydrogen set free by the current in the previous experiment.

Joule made similar experiments on the decomposition of dilute sulphuric acid, sulphate of copper, and sulphate of zinc; and, regarding the difference in the quantity of heat evolved when the current traversed a circuit completely metallic, and when the metallic circuit was broken by the interposition of an electrolyte, as the heat absorbed by the separation of the elements of the electrolyte, he obtained numbers which agree very fairly with those found by other experimenters for the heat evolved in the union of the same elements, as shown in the following table, which gives the quantities of heat evolved or absorbed in the oxidation or reduction of 1 gramme of each metal, according to various experimenters.

	Joule.	Dulong.	Andrews.	Favre and Silbermann.	Grassi.	Woods.
Copper .	594	. .	600	655	. .	611
Zinc . .	1185	1297	1315	1277	. .	1307
Hydrogen .	33553	34587	33808	34462	34666	

The proposition in question has also been confirmed by experiments of another kind. Thus, for instance, by determining the heat evolved when different metals were dissolved in water or dilute acid, Woods found that it was less than that which would be produced by the direct oxidation of the same metals, by a quantity equal to that which would be obtained by burning the hydrogen set free, or which was expended in decomposing the water or acid; and therefore that, when this latter quantity was added to his results, they agreed with the numbers given by experiments of direct oxidation. The quantities of heat evolved by 1 gramme of the several metals, when augmented by that corresponding to the decomposition of the water or acid, were as follows:—

Metal.	Heat by solution of 1 gramme.	Metal.	Heat by solution of 1 gramme.
Sodium . . .	3293	Tin . . .	595
Potassium . .	1745	Lead . . .	256
Zinc . . .	1307	Mercury . .	118
Iron . . .	1204	Silver . . .	96
Copper . . .	611	Bismuth . .	95·5

Indirect methods of determining Heat of Combination.—Assuming the truth of the proposition that in the decomposition of a compound as much heat is absorbed as is liberated in its formation, it is obvious, from the foregoing examples, that the calorimetric effect of a given chemical change can be calculated if the effects of all those which occur simultaneously with it are known. Upon this principle, which is merely that adopted by Woods in the experiments described in the last paragraph, Favre and Silbermann have made a very extensive series of determinations of the quantities of heat evolved in reactions which could not have been easily investigated directly. Their experiments were made with the mercurial calorimeter, and the heat due to a given process was in some cases deduced from two distinct reactions. Thus, the heat of formation of oxide of zinc was deduced (1) from the solution of metallic zinc in dilute sulphuric acid, (2) from the solution of zinc in dilute hydrochloric acid. For the purposes of calculation, the former reaction was considered as consisting in the formation of oxide of zinc, with simultaneous decomposition of water, $Zn^2 + H^2O = Zn^2O + H^2$, and in the subsequent formation of sulphate of zinc by the action of this oxide on the dilute sulphuric acid, $Zn^2O + H^2SO^4 = H^2O + Zn^2SO^4$. The heat absorbed by the calorimeter during the solution of 1 gramme of zinc was 567·9 gramme-degrees: this, according to the supposition, represented the heat of oxidation of the zinc + the heat of formation of sulphate of zinc from anhydrous oxide and dilute sulphuric acid − the heat absorbed by the decomposition of water. Calling the heat of oxidation of one gramme of zinc x, and calculating, from the direct determinations previously recorded, the calorimetric effects of the other processes, we have

$$x = 567{\cdot}9 + 1060{\cdot}4 - 335{\cdot}5 = 1292{\cdot}8.$$

Similarly, when 1 gramme of zinc was dissolved in dilute hydrochloric acid, 503·8 units of heat were absorbed by the calorimeter, and the following equation was obtained to represent the heat of oxidation of that weight of zinc:

$$x = \underset{\substack{\text{Heat absorbed}\\ \text{by calorimeter.}}}{503{\cdot}8} + \underset{\substack{\text{Heat absorbed}\\ \text{by decomposition}\\ \text{of water.}}}{1060{\cdot}4} - \underset{\substack{\text{Heat evolved by}\\ \text{action of dilute}\\ \text{hydrochloric acid on}\\ \text{oxide of zinc.}}}{274{\cdot}3} = 1289{\cdot}9;$$

a result which agrees almost exactly with the foregoing.

This number having been obtained, the heat of oxidation of metallic copper could be deduced in a similar manner from the quantity of heat set free when a known weight of zinc was dissolved in a solution of sulphate of copper. In this way the number 684 was found for the heat of oxidation of 1 gramme of copper.

The following table gives the heats of combination of one equivalent of several metals with one equivalent of various metalloids, deduced from experiments of this kind:—

Metals.	Units of heat evolved by combining with				
	8 grammes oxygen.	35·5 grammes chlorine.	80 grammes bromine.	127 grammes iodine.	16 grammes sulphur.
Hydrogen . .	34462	23783	9322	−3606	2741
Potassium . .	76238*	100960	90188	77268	45638
Sodium . . .	73510*	94847			
Zinc . . .	42451	50296	. .	. .	20940
Iron . . .	37828	49651	. .	. .	17753
Copper . . .	21885	29524	. .	. .	9133
Lead . . .	27675	44730	32802	23208	9556
Silver . . .	6113	34800	25618	18651	5524

Taking the heat developed in the formation of any given compound as a measure of the energy of the affinity of its constituents, a certain definiteness and precision of meaning are given to such terms as strong and weak, active and inert, which are often used in reference to chemical reagents in rather a vague sense; and on comparing the numbers representing the heats of formation of various compounds, they will be found to bear out in a general way the manner in which such terms are commonly applied. The results recorded in the above table, for instance, serve to explain certain facts which have often been quoted as anomalous and opposed to the commonly received idea that the affinities of chlorine are stronger than those of bromine or iodine, and the affinities of bromine stronger than those of iodine. The facts referred to are such as these: the observation of Fehling that in the fractional precipitation of a solution containing both chlorides and bromides with nitrate of silver, the whole of the bromine is contained in the first portions of the precipitate; the similar observation of Field (Chem. Soc. Qu. J. x. 234), and the decomposition of chloride of silver when brought in contact with an aqueous solution of bromide or iodide of potassium, described by the same chemist; and particularly the violent decomposition of chloride of silver, attended with evolution of heat, which takes place, as observed by Deville (Ann. Ch. Pharm. ci. 198), when aqueous hydriodic acid is poured upon it.

The precipitation of bromide or iodide of silver, to the exclusion of the chloride, in cases of fractional precipitation with nitrate of silver, and the conversion of chloride of silver into bromide or iodide by contact with an aqueous solution of iodide of potassium, may be considered as essentially the same phenomenon. When the latter transformation is expressed by an equation, the substances whose formulæ appear in the left-hand member of the equation are those which suffer decomposition; while those which are formed appear on the right-hand side; and on comparing the calorimetric values of the several terms, making due allowance for their state of solution or otherwise, we find that the sum of the calorimetric values on the left-hand side of the equation is less than the sum of the calorimetric values of the substances on the right-hand; thus indicating that, although the conversion of chloride of silver into bromide or iodide by simple substitution would be attended with absorption of heat, the combined effect of all the actions which take place in the experiments under consideration is to cause an evolution of heat.

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* These numbers represent the formation of aqueous solutions of potash and soda: all the rest refer to anhydrous compounds.

Thus we have

$$\begin{array}{lccc} & \mathrm{AgCl} + \mathrm{KBr} & = & \mathrm{AgBr} + \mathrm{KCl} \\ \text{Calorimetric values} & \underbrace{34800 \quad 85678} & & \underbrace{25618 \quad 97091} \\ \text{Sums:} & 120478 & & 122709 \end{array}$$

therefore: heat evolved in the reaction = 122709 – 120478 = 2231 gramme-degrees.

$$\begin{array}{lccc} & \mathrm{AgCl} + \mathrm{KI} & = & \mathrm{AgI} + \mathrm{KCl} \\ \text{Calorimetric values} & \underbrace{34800 \quad 72479} & & \underbrace{18651 \quad 97091} \\ \text{Sums:} & 107279 & & 115742 \end{array}$$

therefore: heat evolved in the reaction = 115742 – 107279 = 8463 gramme-degrees.

Similarly, for the reaction of aqueous hydriodic acid on chloride of silver, we have:

$$\begin{array}{lccc} & \mathrm{AgCl} + \mathrm{HI} & = & \mathrm{AgI} + \mathrm{HCl} \\ \text{Calorimetric values} & \underbrace{34800 \quad 15004} & & \underbrace{18651 \quad 40192} \\ \text{Sums:} & 49804 & & 58843 \end{array}$$

therefore: heat evolved in the reaction = 58843 – 49804 = 9039 gramme-degrees.

The heat evolved in a considerable number of processes of oxidation has been indirectly determined by Favre (J. Pharm. Chim. [3] xxiv. 241, 311, 412; Jahresber. 1853, pp. 22 *et seq.*), for the most part by effecting the oxidations in presence of water in the mercurial calorimeter, by means of hypochlorous acid, whose heat of formation, calculated for one equivalent of chlorine, he found by preliminary experiments to be – 7370 units.

For the details of this investigation we must refer to the original papers; the most important results obtained are as follows, calculated always for one equivalent of the element operated upon.

Substance.	Product.	Heat evolved.	Ratio.	
Yellow phosphorus Red phosphorus	Aqueous phosphoric acid .	209476 181230	4·36	1·49
Yellow phosphorus .	Phosphoric anhydride .	190490		
„ „ . .	Phosphorous acid . .	140394	2·91	1·
„ „ . .	Hypophosphorous acid .	48302	1·	
Arsenic . . .	Arsenic acid . . .	110787	1·54	
„ . . .	Solid opaque arsenious acid	75363		
„ . .	Dissolved opaque arsenious acid . . .	71690	1·	
Phosphorus . . .	Pentachloride . . .	100373		
„ . . .	Trichloride . . .	94804		
Arsenic . . .	Trichloride . . .	71883		
Nitrogen . . .	Nitrous oxide . . .	–8724		
Nitric oxide . . .	Nitric acid . . .	20655		
Nitrous acid . . .	„ „ . . .	27269		
Sulphurous acid . .	Sulphuric acid . . .	27839		
Sulphur (portion of flowers of sulphur insoluble in sulphide of carbon) . .	„ „ . . .	64110		
Plastic sulphur . .	„ „ . . .	67211	3·32	1·71
Sulphur (precipitated from hyposulphite of sodium) . .	„ „ . . .	63407		
Sulphur . .	Sulphurous acid (Favre and Silbermann) .	39373	1·95	1·
Sulphur . . .	Hyposulphurous acid .	20233	1·	
Selenium . . .	Selenious acid . .	23206	1·	
„ . . .	Selenic acid . . .	36360	1·56	
Oxalic acid . . .	Carbonic anhydride . .	30140		
Carbon . .	Carbonic oxide (Favre and Silbermann) . .	14838	1·	
„	Oxalic anhydride . .	33410	2·25	
„	Carbonic anhydride (Favre and Silbermann) .	48480	3·27	
Chlorine . . .	Chloric anhydride . .	–65234		

It is obvious that, even supposing the principle upon which these indirect determinations are made to be quite correct, and all the interfering circumstances to have been taken into account, the results arrived at cannot be of the same degree of accuracy as those obtained by more direct methods: for the total uncertainty attaching to all the independent data from which they are deduced will be accumulated upon them. Moreover, although a comparison of the heat of chemical action, as determined directly, with that deduced indirectly, generally shows, in the simple cases in which it is possible to institute such a comparison, a degree of agreement which may be taken as a confirmation of the correctness of the principles whereby the calculated result is arrived at, and as proving that, at least in these cases, no modifying circumstance of any great importance has been overlooked in the calculation, still it cannot be considered as proved by existing experiments that the cold of decomposition is *always* equal to the heat of combination. On the other hand, it seems probable, on general grounds, that the calorimetric effect of a given chemical process is not an absolutely constant quantity, but that it is to some extent dependent on accompanying physical conditions. In particular, it seems likely that it must vary more or less with the temperature at which the chemical action takes place, and therefore—to take a particular example—that the heat *evolved* by the combination of mercury with oxygen, at a comparatively low temperature, is not equal to the heat *absorbed* by the decomposition of oxide of mercury at a higher temperature. The equality of these two quantities of heat would involve also the equality of the specific heat of oxide of mercury with the sum of the specific heats of its elements; otherwise, the quantity of heat needed to raise the temperature of a given quantity of mercury and oxygen from the ordinary temperature to a temperature above that at which oxide of mercury is decomposed, would be different, if the two substances remained uncombined during the process, from what it would be if they first entered into combination and afterwards separated again; and since the final condition of the mercury and oxygen would be the same in each case, the difference between the quantities of heat would have disappeared without producing any apparent effect. In the particular case that has been taken as an example, it is possible that the specific heats of the elementary bodies are together equal to the specific heat of the compound, or that the difference may be compensated by the difference in the latent heats of vaporisation of oxygen at the temperature of combination and at that of decomposition. But, although this may be the case, experimental proof that it is so is still wanting; and even if it were afforded here, or for any other particular substance, there would still not be sufficient warrant for assuming as a generally established fact that the cold of decomposition is equal to the heat of combination, independently of the conditions under which these processes respectively occur. In connection with these considerations, it is perhaps worth while to draw attention to the fact that the heat of combustion of hydrogen, deduced by Joule from the electrolysis of water at the ordinary temperature, is decidedly less than that found by other experimenters who determined directly the heat of combustion at a high temperature (see p. 114). These experiments are perhaps not sufficiently comparable in other respects to justify us in attaching much importance to this result; but, taking it as it stands, it is in harmony with the fact that the specific heat of water-vapour is less than the sum of the specific heats of its constituents.

The laws by which Thomsen considers that the development of heat in chemical action is governed, appear to involve views similar to those above explained. The fundamental propositions assumed by him are as follows:—The intensity of the chemical energy of the same body at a constant temperature is unchangeable; the whole quantity of heat developed in a given chemical action is a measure of the chemical energy therein exerted, and is proportional to the difference between the total chemical energy of the reagents and the total chemical energy of the products.

Heat produced by Chemical Decomposition.—There are a few phenomena which are, at least apparently, exceptions to the general rule that heat is evolved in combination and absorbed in decomposition. It was found, for instance, by Favre and Silbermann, that charcoal evolves more heat by burning in nitrous oxide than by burning in pure oxygen. The excess of heat in this case could only be due to heat evolved in the decomposition of the nitrous oxide, and direct experiments proved that this decomposition was attended with evolution of heat. They found further that heat is produced in the decomposition of peroxide of hydrogen by platinum, and from the experiments of Favre, already recorded, it appears that heat is absorbed in the oxidation of chlorine to hypochlorous or to chloric acid. Perhaps these and similar phenomena may be brought into harmony with the general rule, by taking into consideration the evolution of heat due to the combination of two similar atoms to form a molecule, and the corresponding absorption of heat due to the separation of the atoms constituting a molecule of an elementary body.

The influence of high temperature in promoting chemical action—as, for instance between oxygen and hydrogen, which combine when heated, but are without action on each other in the cold—is not an exception of the kind here referred to. It is rather a thermometric than a calorimetric phenomenon; high temperature being a favourable condition for chemical action in these cases, but in no way its cause. At very low temperatures chemical action appears in all cases to be much retarded: as one illustration, it may be mentioned that when liquefied ammonia, cooled to about −65°, is poured upon concentrated sulphuric acid, the two liquids form separate layers, and for some time no action takes place between them (Loir and Drion). Phosphorus and iodine, which combine energetically and with vivid combustion at common temperatures, may be shaken together in a tube cooled by a freezing mixture, without exerting the slightest action on each other.

5. *Relations of Heat to Electricity.*

Electricity produced by Heat.—*Pyro-electricity developed in Crystals.*—To what has been already said on this subject in the article Electricity (ii. 411) we have only to add the results arrived at by Gaugain (Ann. Ch. Phys. [3] lvii. 5) in reference to the pyro-electricity of tourmalines. He finds that this phenomenon obeys the following laws:—(1.) When any number of tourmalines are united by their poles of the same name, they form a battery which produces, under any given circumstances, a quantity of electricity exactly equal to the sum of the quantities which the several tourmalines would produce separately under the same circumstances.

(2.) When several prisms of equal section are superposed, the quantity of electricity developed by the combination is merely equal to that which would be furnished, under the same conditions, by any one of the prisms taken separately.

(3.) The quantity of electricity produced by a prism of tourmaline is proportional to its sectional area, and is independent of its length.

(4.) The quantity of electricity which a tourmaline developes when its temperature is lowered a given number of degrees, is independent of the length of time in which the cooling is effected.

(5.) When a tourmaline is heated a given number of degrees, the quantity of electricity developed is precisely the same as that which would be produced if it were cooled to an equal extent.

Gaugain finds that the development of electricity, consequent on the alteration of the temperature of a tourmaline, is very much more marked if one pole of the crystal is placed in electric communication with the earth, than when the crystal is completely insulated.

Thermo-Electricity.—When two bars of dissimilar metals are soldered together at each end, a continuous current of electricity circulates through the circuit formed by them, as long as the two soldering points are at different temperatures, the direction of the current being reversed according as one or the other of these points is the hotter. The electro-motive force (Electricity, ii. 459) developed at each soldering point is directly in proportion to its absolute temperature (p. 52), and therefore, since the electro-motive force developed at one end is contrary to that developed at the other, the resultant electro-motive force of the whole circuit is proportional to the difference between the temperatures of the soldering points. (Clausius, Thomson.) (See further, ii. 412, 413.)

Heat produced by Electricity.—The laws regulating the development of heat by the sudden discharge of frictional electricity, or electricity of high tension, have already been treated of in the article Electricity (ii. 395), and in the same article (p. 470) it has been shown that the heat produced by a continuous current of electricity is the exact equivalent of the chemical action whereby the current is generated. In the application of this rule, the total chemical action throughout the circuit must be taken into account, electrolytic decomposition being counted positive or negative according as the direction of the current which would be generated by it, were it to take place independently of the battery, is the same as that of the battery or the contrary. As further explained in the article referred to, the heat developed by an electric current is related to the intensity of the current and to the resistance of the circuit in the manner expressed by the formula:

$$H = I^2R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

where H represents the heat, I the intensity of the current, and R the resistance. Putting E for the electro-motive force, we have, by Ohm's formula (ii. 459):

$$I = \frac{E}{R},$$

and therefore the above equation (a) may be written:

$$H = IE \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

From this it follows that, by diminishing the resistance of the circuit, the electro-motive force remaining the same, the total heat, H, can be augmented indefinitely, the intensity, and therefore also the chemical action in the battery, increasing in proportion to the diminution of resistance. But in any single portion of the circuit, whose resistance is r, the development of heat will attain a maximum for a particular value of r. The heat produced in this part will in fact be $h = I^2r = \frac{E^2}{(R+r)^2}r$, the value of which last expression reaches a maximum when $R = r$, R being the constant resistance of the remainder of the circuit, including the battery. Hence, in order that as large a proportion as possible of the whole heat of the circuit may be generated in the conducting wire, and as small a proportion as possible in the battery, the internal resistance, R, of the battery must be equal to the resistance, r, of the remainder of the circuit. And, since the heating power of the current represents its total energy, it follows that the same proportion between the internal and external resistance of the circuit is the most advantageous that can be adopted for causing the current to produce changes of any other kind outside the battery.

Thermal phenomena of a particular kind occur when an electric current, instead of traversing a homogeneous conductor, passes from one substance to another. Then, in addition to the development of heat corresponding to the resistance of the conductor, according to the laws stated in the last paragraph, a further development or absorption of heat takes place, depending upon the direction of the current. If the current crosses the point of junction of two dissimilar portions of the circuit, in the same direction as the thermo-electric current which would be generated by the application of heat to this point, then the heat developed there is less than corresponds to the resistance of that portion of the circuit, or, in other words, heat is absorbed; if the current passes the point of junction in the opposite direction, the heat generated is more than what corresponds to the resistance.

With a junction formed of the same two metals, the development or absorption of heat thus occasioned is proportional to the intensity of the current by which the junction is traversed. With combinations of different metals, the extent to which this phenomenon occurs varies with the positions of the metals in the thermo-electric series (ii. 412), being greatest for those combinations which give the most intense thermo-electric currents.

6. *Relations of Heat to Mechanical Energy.*

In preceding parts of this article, we have seen that increase of volume and of elastic force are among the most universal of the effects of heat. In this way heat is constantly producing motion, and when this motion is concentrated in a given solid body, and a definite direction is given to it, as in the steam-engine, heat becomes by far the most important artificial source of mechanical power that we possess. Conversely, innumerable familiar facts supply us with illustrations of the production of heat at the expense of mechanical power. Thus, in all machines there is a certain loss of power, the work performed by the machine never representing the full mechanical equivalent of the power needed to drive it. That portion of the mechanical energy supplied to the machine which is wasted, so far as the performance of useful work is concerned, is expended in overcoming the passive resistances by which the motion of the machine is opposed; such, for instance, as friction between contiguous surfaces not moving with the same velocity, or the rigidity of straps or cords used to transmit movement from one part to another. But, whenever motion is produced in opposition to friction, or a rigid body is forcibly bent, heat is generated; the mechanical energy expended in producing these effects is lost to the purposes of the machine, but the heat evolved is its representative. Percussion is another means by which mechanical power can be destroyed and heat generated in its stead. These and similar facts have long attracted the attention of philosophers, and great importance has been attached to them in reference to most of the theories that have been suggested from time to time to explain the nature of heat and the effects which it produces. The following is a quotation from Black's *Lectures on Chemistry* (vol. i. pp. 31, 32), and relates to Bacon's investigations into the nature of heat contained in his treatise *De formâ Calidi*:—

"The only conclusion, however, that he" (Lord Verulam) "is able to draw from the whole of his facts, is a very general one, viz. that heat is motion.

"This conclusion is founded chiefly on the consideration of several means by which heat is produced, or made to appear, in bodies; as the percussion of iron, the friction of solid bodies, the collision of flint and steel.

"The first of these examples is a practice to which blacksmiths have sometimes recourse for kindling a fire; they take a rod of soft iron, half an inch or less in thickness, and, laying the end of it upon their anvil, they turn and strike that end very quickly on its different sides, with smart blows of a hammer. It very soon becomes red hot, and can be employed to kindle shavings or wood, or other very combustible matter.

"The heat producible by the strong friction of solid bodies, occurs often in some parts of heavy machinery, when proper care is not taken to diminish that friction as much as possible, by the interposition of lubricating substances; as in the axles of wheels that are heavy themselves, or heavily loaded. Thick forests are said to have taken fire sometimes, by the friction of branches against one another in stormy weather. And savages, in different parts of the world, have recourse to the friction of pieces of wood for kindling their fires. . . . .

"The third example above adduced in the collision of flint and steel, is universally known.

"In all these examples, heat is produced or made to appear suddenly, in bodies which have not received it in the usual way of communication from others, and the only cause of its production is a mechanical force or impulse, or mechanical violence."

From these and many other similar phenomena, it is abundantly clear that, by the expenditure of heat, mechanical work can be effected, and that heat can be produced by the expenditure of work. Dismissing, therefore, for the present, all considerations as to the ultimate nature of heat, we may say that heat and work are mutually convertible, and we have in this section to consider the conditions which regulate the transformation of one of these forms of energy into the other.

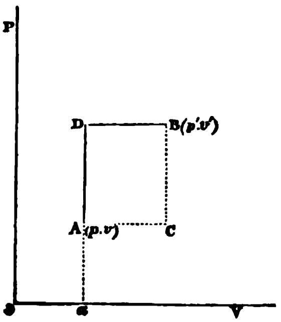
Work produced by Heat.—The measure of the work done by heat, when it causes expansion, is obviously the product of the resistance overcome into the space through which the expansion takes place; that is, if r denote the resistance, and v and v' the initial and final volumes of the body which undergoes expansion, the work done by the heat will be represented by

$$A = r(v' - v).$$

In estimating the resistance by which the expansion of a given body is opposed, it is needful to take into account, not only the external pressure upon its surface, but also, as has been already pointed out (pp. 40 and 73), the molecular forces which tend to maintain unaltered the relative positions of its ultimate particles. The work, A, performed by heat when it causes expansion, must therefore be considered as made up of the *internal work*, a_i, performed in opposition to internal molecular forces, and the *external work*, a_e, expended in overcoming external pressure. In solid and liquid bodies the ratio, $\frac{a_i}{a_e}$, of the internal to the external work is very considerable, but in a perfect gas, the resistance to expansion arising from the mutual attractions of the molecules is insensible, and therefore also the expenditure of work in overcoming this resistance is insensible: hence, in this case $\frac{a_i}{a_e} = 0$, or $a_e = A$. But since it is the external work only which is available for the production of external effects, the consideration of the transformation of heat into mechanical energy is much simpler in the case of gases than in that of liquid or solid bodies; it is further much the most important practically, for although the heat employed in the performance of internal work upon solids or liquids is not necessarily lost ultimately, it is, for the time at least, totally unavailable. We may perhaps compare the transformation of heat into work with the commercial transformation of labour into wealth: then, a perfect gas will represent a medium of transformation comparable with an industrial process which requires no previous expenditure on the part of the workman to enable him to exchange his labour for wages; while a solid or liquid will represent a medium of transformation comparable with a process which can only be carried out by the previous investment of a considerable capital. The capital thus "sunk" may be realised again at some future time, but it represents a certain quantity of labour, which, for the time being, cannot be transformed into wealth.

In order that work may be continuously performed by heat, it is not enough that a portion of air or other gas should be expanded once for all in a cylinder closed by a piston, or in any other similar apparatus. It is true that motion would be thus produced, and that this might be the full equivalent of the heat expended, but the process would soon come to an end. Practically, the extent to which a gas can be expanded so as to produce motion, is very limited, both by the size of the apparatus that can be used and by the temperatures that are attainable. In order that the process may be continuous, the action of the machine, by means of which the transformation is effected, must be periodic: after a certain cycle of changes, all its parts must return to the same relative positions and condition as they had at first, and the air or gas must return to its original pressure and temperature. Such a cycle might evidently be repeated indefinitely, and if any transformation of heat into work were effected by it, the same amount of transformation would take place each time the cycle was completed. At pages 50 and 51, we saw that in the passage of a gas through a succession of conditions, with respect to temperature, pressure, and volume, which can be represented graphically by a rectangle, and are such that the final state of the gas is the same as its state at the beginning of the process, a certain quantity of heat is expended, which is proportional in amount to the area of the rectangle representing the succession of changes; but it was not there explained what becomes of the heat thus expended.

Fig. 547.



Returning to the consideration of this case, and using the same notation as before, it is plain that, during the passage of the gas from the state A to the state B, through the intermediate stages represented by the lines AD, DB, a quantity of work is performed, which is represented, in kilogramme-metres, by

$$A = p'(v' - v);$$

and that while the gas returns from the condition B to the condition A, along BCA, there is expended a quantity of work represented by

$$A' = p(v' - v);$$

and, therefore, during the whole cycle ADBCA, a quantity of work is ultimately gained equal to

$$A - A' = (p' - p)\,(v' - v).$$

But, by the last equation on page 51, the amount of heat expended at the same time is

$$Q - Q' = \frac{D}{Ha}\,(c' - c)\,(p' - p)\,(v' - v);$$

therefore, between the heat expended and the work produced, there exists a relation expressed by the equation

$$Q - Q' = \frac{D(c' - c)}{Ha}\,(A - A') \quad . \quad . \quad . \quad . \quad (n).$$

If we assume that the difference between the specific heat under constant pressure and the specific heat at constant volume is constant for each gas, and is inversely proportional to its density (a relation which is implied in equation (*a*), p. 42), the coefficient of $(A - A')$ in this expression is constant; we may therefore represent it by $\frac{1}{E}$, and write equation (*n*) thus:

$$Q - Q' = \frac{1}{E}\,(A - A') \qquad \text{or} \qquad E\,(Q - Q') = A - A'.$$

That is to say, the heat expended is proportional to the work performed, and *vice versâ*; so that for each kilogramme-degree of heat expended, a quantity of work is performed equal to E kilogramme-metres.

The value of E can be deduced from equation (*n*) by introducing the numerical values of the constants, namely:

$$H = 10{,}333 \text{ kilogr.}, \qquad a = 0\ 003665, \qquad D = 1{\cdot}293 \text{ kilogr.}$$
$$c' = 0{\cdot}2374, \qquad \text{and } c = 0{\cdot}168 \text{ (p. 42)}.$$

These values give us:

$$E = 423;$$

that is to say, when heat is transformed into work, every kilogramme-degree of heat (1000 of the heat-units hitherto employed in this article) consumed generates 423 kilogramme-metres of work; or, more generally, the heat needed to raise the temperature of any given weight of water from 0° to 1° C., is equivalent to the amount of mechanical energy required to raise 423 times the same weight of water through one metre from the surface of the earth.

The ratio E is therefore called the mechanical equivalent of the unit of heat, and its reciprocal is, as we shall see, the thermal equivalent of the unit of work.

That the relation between the heat expended and the work generated is necessarily constant, whatever the process may be by which one is transformed into the other, results from the following considerations. If by one process a unit of heat could be made to perform E units of work, and by another process $E + e$ units of work could be generated by the same quantity of heat, a portion of the mechanical energy produced in this second process might be expended in reversing the first, so as to regenerate the original quantity of heat: thus by combining the two processes, the first being worked backwards, each unit of heat expended would reproduce itself and e units of work *in addition*; there would thus be generation of mechanical energy without any corresponding annihilation of any other form of energy. (The principle here implied, that a given quantity of work is capable of giving rise to as much heat as is needed for its own production, results from the above equation (n), but it will be further considered in what follows.)

Nevertheless, in consequence of the unavoidable defects of all experimental processes, the values of E deducible by different methods are not exactly equal, but the agreement between them is quite sufficient to establish the fundamental principle of the real constancy of the relation between heat and work. A table giving the results of the most important determinations of this ratio will be found further on under the head **Heat produced by Work.**

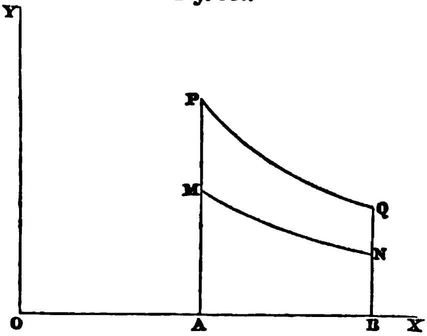
Under all circumstances, the quantity of heat which must be employed in order to effect the transformation of a given amount of it into work considerably exceeds the quantity transformed. In the example above considered, the total quantity of heat imparted to the gas was Q; but of the work, A, generated by this amount of heat during the passage of the gas from the state A to the state B, a certain portion, A', was employed, during the return of the gas to its initial state, in regenerating the quantity of heat Q'. The useful work performed was, therefore, $A - A'$, and the quantity of heat transformed was $Q - Q'$, and the ratio of this to the total heat employed, namely, $\frac{Q - Q'}{Q}$, represents the efficiency of the process of transformation, or the value of the engine in which it takes place as a source of mechanical power. The maximum value which this fraction is capable of attaining, depends on the range of temperature passed through by the fluid which is the medium of transformation. This can be most easily demonstrated in a case where the changes of the volume of the gas take place at constant temperatures; that is, where it is kept at one temperature during the whole process of expansion and at another during the whole process of contraction.

These conditions are approximately realised practically in the **air-engine** invented by the Rev. Robert Stirling, in 1816. This engine consists essentially of two cylinders; a larger one to which the heat is applied, which we may call, for distinction, the heating cylinder, and a smaller one, which may be called the working cylinder, wherein the tranformation of heat into work takes place. The bottom of the working cylinder is connected by a pipe without a valve with the top of the heating cylinder. Within the heating cylinder is a plunger, composed of non-conducting materials, which occupies nearly half its length, and between it and the sides of the cylinder are passages by which the air can pass from one end to the other when the plunger is raised or lowered. In the working cylinder is a piston which fits it air-tight; this piston and the plunger of the other cylinder are both attached by connecting rods to cranks fixed to the same axle, but making an angle of ninety degrees with each other. The heating cylinder is closed at the top, and the rod from which the plunger hangs passes through an air-tight stuffing box; the working cylinder is open at the top. Heat is applied to the bottom of the heating cylinder, and the upper part is kept cool.

The action of the engine is as follows: Suppose the plunger to be at the top of the heating cylinder, and consequently, the piston in the working cylinder in the middle of its stroke; then, if heat is applied to the bottom of the heating cylinder, the air contained there below the plunger will be expanded, and will press the piston upwards; but the motion of the piston being communicated through the axle to the plunger, the latter will descend, and displacing the heated air from the bottom of the heating cylinder, drive it into the cool space at the top. The elastic force of the air being thus diminished, the piston will be forced down by the pressure of the air upon its upper surface; the plunger now returning to the top of the heating cylinder, the air will be driven to the bottom, where it will be again heated, and the piston will be again forced up by its expansion. Thus by the alternate heating and cooling of the same quantity of air, the motion of the engine is kept up.

In consequence of the manner in which the piston and plunger are respectively connected with the axle, each attains its maximum velocity while the other is at rest, so that the action of the engine during one revolution may be considered as essentially made up of four periods: in the first, the temperature of the air is raised, its volume remaining the same, and consequently its pressure increasing; in the second, the air expands, performing work, but so much heat is imparted to it during the expansion, that its temperature remains constant; in the third period, the temperature of the air is reduced to what it was at the beginning of the first period, its volume being unaltered, and therefore its elastic force being diminished; and in the fourth, it is compressed to its original volume, the heat generated by the compression being withdrawn, so that the air remains at the same temperature throughout the whole process. These four successive operations, constituting together one cycle in the action of the engine, may be represented by a diagram such as *fig.* 548, where the abscissa O A represents the volume v_0, of a unit of weight of air at the initial temperature t_0, and the ordinate A M represents the corresponding pressure p_0. The air is first heated, without change of volume, from the temperature t_0 to the temperature t_1; during this operation, its elastic force increases to p_1, represented in the diagram by the ordinate A P; and to effect this change a quantity of heat equal to $c(t_1 - t_0)$ must be imparted to it, c being the specific heat of air at a constant volume; but as no expansion takes place, no work is performed. Next, the air expands from the volume v_0 to the volume v_1, represented by the abscissa O B. Since the temperature of the air is kept constant while it expands, the pressure varies inversely as the volume, a relation represented by the hyperbolic arc P Q, so that the final pressure of the expanded air is represented by the ordinate B Q. During this operation, external work is performed, which is obviously proportional to the area A P Q B, contained between the arc P Q, the axis of abscissæ, and the two ordinates A P and B Q. But in order to prevent the cooling of the gas during its expansion, a quantity of heat, q, must be given to it, of which the mechanical equivalent is exactly the external work which this area represents. In the third operation, the air is cooled to its initial temperature t_0, its volume remaining unaltered, and therefore no work being generated or expended. The pressure is thus reduced from B Q to B N, and a quantity of heat requires to be withdrawn equal to $c(t_1 - t_0)$. Lastly, the air is compressed, while kept at the constant temperature, t_0, to its original volume v_0. To effect this, work must be expended and heat must be removed from the air. The relation between volume and pressure being represented by the hyperbolic arc N M, the work needed for the compression of the air is represented by the area A M N B, and is precisely the mechanical equivalent of the quantity of heat, q', which must be withdrawn from the air in order to maintain its temperature constant during the process.

Fig. 548.



Accordingly, during the first two operations, the air receives a quantity of heat equal to $c(t_1 - t_0) + q$, and developes a quantity of external work geometrically represented by the surface APQB. In the two following operations the air loses a quantity of heat equal to $c(t_1 - t_0) + q'$, and there is expended a quantity of work geometrically represented by the surface AMNB. The ultimate useful expenditure of heat is, therefore, $q - q'$, and the available quantity of work generated is represented by the area MPQN, or the difference between APQB and AMNB. The total expenditure of heat, during the complete cycle of operations, is q; the quantity q' given out by the air during its compression at the temperature t_0 cannot in any way be made available for the maintenance of the action of the machine, and may therefore be considered as entirely lost. The quantity of heat $c(t_1 - t_0)$, which the air gives out when cooled from the temperature t_1 to the temperature t_0, may, on the contrary, be employed to heat another quantity from t_0 to t_1, and, therefore, does not make part of the ultimate expenditure. The reason why this portion of heat can be recovered, while the quantity q' cannot, is, that it is heat of a higher temperature, whereas q', being heat of the temperature t_0, is useless for heating any body to a temperature higher than t_0. The ratio of the useful expenditure of heat to the total expenditure is, therefore, $\frac{q - q'}{q}$.

The values of the quantities q and q' can be found as follows:—representing the mechanical equivalent of heat by E, we have, as a consequence of the above discussion,

$$Eq = \text{surf. APQB, and } Eq' = \text{surf. AMNB},$$

and consequently

$$\frac{q - q'}{q} = \frac{\text{surf. APQB} - \text{surf. AMNB}}{\text{surface APQB}}.$$

But PQ and MN, being each an arc of a rectangular hyperbola of which the lines of no volume and no pressure, OY and OX, are the asymptotes, it follows that the surface

APQB is to the surface AMNB as AP to AM. Therefore, $\frac{q - q'}{q} = \frac{\text{AP} - \text{AM}}{\text{AM}} = \frac{p_1 - p_0}{p_1}$. But p_1 and p_0 are the pressures exerted by the same mass of gas, under the same volume, v_0, at the two temperatures t_1 and t_0; consequently, $\frac{p_1}{p_0} = \frac{a + t_1}{a + t_0}$ (by equation *b*, p. 45), and—

$$\frac{q - q'}{q} = \frac{p_1 - p_0}{p_1} = \frac{(a + t_1) - (a + t_0)}{a + t_1} = \frac{\tau_1 - \tau_0}{\tau_1},$$

τ_1 and τ_0 representing the absolute temperatures (see p. 52) corresponding to the centigrade temperatures t_1 and t_0.

A similar investigation of any other engine in which work is generated by the expenditure of heat in causing the alternate expansion and contraction of a gas, would lead to the same expression for its maximum efficiency; hence, in every air-engine, whatever its mode of action, provided no heat is spent uselessly in causing changes of temperature, the ratio of the useful expenditure of heat to the total expenditure is equal to the difference of the absolute temperatures between which the engine works, divided by the highest of these temperatures.

The agreement of this theoretical deduction with the results of practical experience, is one of the most conclusive arguments that can be brought forward in favour of the view which regards heat as a mode of energy convertible into mechanical energy, and in opposition to the older view, according to which heat is regarded as an indestructible entity, and the production of mechanical energy by it, as depending upon its transference from a hotter to a colder body. According to this latter theory, the efficiency of an air-engine ought to be much greater than that of a steam-engine,—a conclusion which has not, however, hitherto been confirmed in practice. Taking a special example, the quantity of heat transformed into work, compared with the total heat supplied to a steam-engine, might be calculated upon this theory, as follows:—Let the engine be supposed to be worked at a pressure of 5 atmospheres, and consequently at the temperature 152°. Each kilogramme of saturated steam supplied to the cylinder at this temperature requires for its formation, according to Regnault's experiments (p. 97), 653 kilogramme-degrees of heat, *minus* the heat contained in the water with which the boiler is fed. If we suppose the engine to be worked expansively, down to the pressure of the atmosphere, and that the steam remains saturated during the expansion, it will escape into the atmosphere with the temperature 100°, and when cooled again to the temperature t, of the water supplied to the boiler, each kilogramme will give out $637 - t$ kilogramme-degrees of heat: under these conditions, therefore, the steam only loses, during its expansion in the engine, $(653 - t) - (637 - t) = 16$ degrees of heat out of the whole quantity contained in it. If t, the initial temperature of the water, be 10°, for example, 643 kilogramme-degrees of heat will have been required to generate each kilogramme of steam, and the fraction $\frac{16}{643}$, or not quite $\frac{1}{40}$, will represent the proportion of the total heat which has been converted into mechanical energy. The value of this fraction may be increased somewhat by adding a condenser to the engine, so as to obtain a greater range of expansion. If, for example, the temperature of the condenser is 40°, and the steam expands in the cylinder until its tension is the same as that in the condenser, or 55 millimetres, conditions which are never quite attained in practice, the quantity of heat given up to the condenser by each kilogramme of steam will be $619 - 40 = 579$ kilogramme-degrees; and if the boiler is fed with the condensed water at the temperature 40°, the formation of this quantity of steam will have required $653 - 40 = 613$ kilogramme-degrees. In this case, therefore, $613 - 579 = 34$ parts of heat will be converted into work out of every 613 parts imparted to the boiler: accordingly $\frac{34}{613}$, or very nearly $\frac{1}{18}$, will be the fraction representing the efficiency of the engine.

This calculation (borrowed from Regnault, Mém. Acad. Sciences, xxvi. introd. pp. v. vi.), it will be observed, supposes that all the heat which is not regained in the condenser, or contained in the steam which escapes into the atmosphere, has been converted into work: nevertheless, the efficiency of the engine comes out much below what is actually attained in practice. By careful experiments on large engines, of upwards of 100 horse-power, in which the loss of heat by radiation and conduction, or by other accidental causes, was estimated and allowed for, as accurately as possible, Hirn found that the difference between the quantity of heat supplied to the boiler, and that absorbed by the condenser, amounted to between $\frac{1}{10}$ and $\frac{1}{8}$, on an average to about $\frac{1}{8}$, of the former quantity. Practically, therefore, the steam engine is between twice and three times as efficient a machine as would appear from the above calculation.

The key to this contradiction between theory and practice, lies in a false assumption that has been made in the calculation. It was assumed that, when saturated steam expands in the cylinder of a steam-engine, it remains in the state of saturated steam, and the heat contained in it was estimated, in accordance with this supposition, from Regnault's determinations of the total heat of saturated steam at various temperatures. In fact, however, saturated steam, if it performs external work while expanding, suffers partial condensation at the same time, and the latent heat of vaporisation of the steam which condenses becomes available for the production of work in the cylinder. It is not therefore saturated steam which escapes from the cylinder of an engine working under the conditions we have supposed, but a mixture of steam and water, containing a quantity of heat, less than the total heat of vaporisation of an equal weight of saturated steam at the same temperature by the latent heat of vaporisation of the proportion of water present. The necessity of this condensation was deduced by Rankine in 1849, and soon afterwards by Clausius, as a necessary consequence of the existence of the mechanical equivalent of heat, and shown to be the principal cause of the accumulation of water in unjacketed steam-cylinders, which had long been known as a practical inconvenience in the working of steam expansively. The beneficial effect of employing superheated steam, and of enclosing the cylinder in a steam-jacket, is that the steam can then expand, performing external work, without undergoing liquefaction. The condensation of aqueous vapour, when it does work on expanding, is distinctly seen in the formation of a mist under an air-pump receiver, containing moist air, when the piston of the pump is raised.

The fact that a considerable part of the heat supplied to a steam-boiler is consumed in converting the water into steam, is not therefore a reason why an air-engine, in which no portion of heat is similarly expended in causing a change of state, should be more efficient than a steam-engine; and the investigation of the conditions under which work is generated in the steam-engine leads to the general result, that the efficiency of any heat-engine is independent of the nature of the fluid which is the medium of transformation of heat into work, and which may be air, steam, or any other vapour or gas; but that, supposing the reception of heat to take place wholly at one temperature, and the rejection of heat wholly at another, the heat transformed into mechanical energy, is to the whole heat received by the fluid, as the range of temperature is to the absolute temperature at which heat is received, and that, between given limits of temperature, the maximum efficiency is attained when the reception and rejection of heat take place, in the manner just stated, at the highest and lowest temperatures respectively.

The most conclusive confirmation of this result is that when it is applied to the calculation of the mechanical equivalent of heat from Hirn's experiments on large steam-engines already referred to, the mean number found is 413, which differs by only 2½ per cent. from that deduced at the beginning of this section from the thermodynamic properties of air.

Heat produced by Work.—In the introduction to this article (p. 16), it is pointed out as a general fact that heat may be generated by reversing any of its effects. A process by which heat is made to generate work may, therefore, by reversal, become a process for the conversion of work into heat. But, as mentioned at the place quoted, mechanical energy may be transformed into heat by non-reversible processes, such as its expenditure in friction or percussion. There are also indirect methods of transforming work into heat which cannot be reversed, step by step; for instance, mechanical energy, used to give motion to a magneto-electric machine, can be caused to generate electricity, and this electricity, if not expended in effecting chemical changes or in reproducing mechanical energy, takes the form of heat in traversing the conducting wire, although by applying heat to the homogeneous conductor, electricity could not be regenerated. This, therefore, is an indirect, non-reversible, process of transformation. But it is found that whether the process by which mechanical energy, or work, is converted into heat is direct or indirect, reversible or non-reversible, the quantity of heat generated by a given quantity of mechanical energy expended is, within the limits of experimental error, always the same, and, within similar limits, the same as the quantity of heat required to regenerate the original quantity of mechanical energy.

The simplest mode of transforming work into heat, is perhaps the compression of a gas, by which means, as in the familiar experiment of the fire-syringe, a temperature sufficiently high to inflame easily combustible substances can be produced without difficulty. The generation of heat in this manner can be made a continuous process, by alternately compressing the gas at a high temperature and allowing it to expand at a low temperature. The reversal of the four operations represented by the diagram, *fig.* 547, p. 121, would constitute such a process, and by the application of reasoning such as that previously employed in the consideration of this case, it is evident that the work which it would be necessary to expend, in order to effect this reversal, would be represented by $A - A'$, and that the heat generated thereby would be

$$Q - Q' = \frac{1}{E}(A - A'),$$

E, being as before, the mechanical equivalent of heat.

The expenditure of mechanical energy in compressing liquid and solid bodies is also attended with the production of heat. According to Thomson, the thermal effect of compression may be expressed by the formula:

$$\theta = \frac{\tau a p}{E c},$$

where θ is the effect in question, τ the absolute temperature, a the coefficient of expansion by heat, p the pressure, E the mechanical equivalent of heat, and c the specific heat of the substance. This formula has been verified by Joule (Proc. Roy. Soc. ix. 496) by experiments on water and upon oil, the temperatures varying in the first case between 1·2° C. and 40·4°, and the pressures between 15·64 and 25·34 atmospheres; in the experiments on oil the temperature was always about 17° and the pressures were varied from 7·92 atmospheres to 25·34. In the experiments on water at 1·2°, pressure caused a lowering of temperature instead of a rise, as in the other experiments,—a result which agrees with the fact that water contracts by heat at this temperature. Similarly, when weights are laid upon metallic pillars, heat is evolved, and is absorbed when they are removed, the quantity evolved or absorbed increasing with the weights employed (Joule, *ibid.* viii. 564). Conversely, the stretching of metallic wires causes heat to disappear. Joule found (*ibid.* viii. 355) that an iron wire, ¼ inch in diameter was cooled ⅛ degree C. when stretched by a weight of 775 lb. Similar results were obtained with cast iron, hard steel, copper, and lead. The thermal effects were in all cases found to be almost identical with those deduced from Professor Thomson's theoretical investigation, the particular formula applicable to the case in question being $Q = \frac{\tau a p}{E}$, where Q is the heat absorbed in a wire one foot long, and the other symbols have the same significations as above. Vulcanised india-rubber, which, when stretched, contracts by heat (p. 73), became hotter when the stretching weight was applied, and colder when it was removed. Similar results have been obtained by Edlund, (Ann. Ch. Phys. [3] lxiv. 245), whose experiments lead to the following general conclusions:—

1. When a metal is stretched, without exceeding its limits of elasticity, a cooling effect is produced proportional to the mechanical force employed to stretch it.

2. If the metal afterwards return to the original volume, performing in so doing a quantity of external work equal to that expended in stretching it, it is heated to the same extent as that by which it was previously cooled, and consequently proportional to the mechanical force by which the metal was kept in the stretched state before contracting.

3. If on the other hand, the metal resumes its original bulk without performing external work, it is more strongly heated than in the previous case, and the difference between the two heating effects is proportional to the external work performed, in the one case, by the metal during its contraction.

4. From these three principles, it follows that when a metal passes from the volume V_0 to the volume V_1, without exceeding the limits of perfect elasticity, the accompanying calorific effect does not depend solely upon the initial and final volumes, but also upon the manner in which the entire change takes place.

EXPERIMENTAL DETERMINATION OF THE MECHANICAL EQUIVALENT OF HEAT.—It is obvious that any of the processes whereby work is transformed into heat, or heat into work, may serve for the determination of the numerical ratio existing between the unit of work and the unit of heat, provided the process is such as to admit of the accurate measurement of the work or heat expended and of the heat or work produced. The earliest attempt to ascertain the value of this ratio appears to have been made by Count Rumford. His experiments described in his essay, entitled *An Experimental Inquiry concerning the Source of the Heat which is excited by Friction* (read before the Royal Society, January 25, 1798, and published in the Phil. Trans., also in "*Essays, Political, Economical, and Philosophical*, by Benjamin Count of Rumford," 3 vols. 8vo, Lond. 1798–1802, vol. ii. p. 469), were made by pressing a blunt steel borer against the bottom of a cavity made in a brass cylinder which was caused to revolve, while the borer was kept stationary. Considering the state of opinion at the time as to the probable nature of heat, these experiments, and especially the conclusions drawn from them by their author, are very remarkable, but it is only of late years that they have attracted the attention which they deserve. In the most complete experiment, the brass cylinder was placed inside a wooden box containing 18·77 lb. avoirdupois of water; the temperature of the water at the beginning of the experiment was 60° F., and was found to rise continuously when the cylinder was set in motion, until at the end of 2½ hours the water boiled. Rumford states the results of this experiment in a tabular form, taking account of the weights and specific heats of the brass cylinder and steel borer, and gives the total quantity of heat produced, exclusive of the amount accumulated in the wooden box, and of that which was lost by radiation, as sufficient to raise the temperature of 26·58 lb. of water 180 degrees Fahrenheit, or from the freezing to the boiling point; he then quotes experiments by Crawford and by himself, from which he concludes "that the quantity of heat produced equably, or in a a continual stream (if I may use that expression), by the friction of the blunt steel borer against the bottom of the hollow metallic cylinder, in the experiment under consideration, was *greater* than that produced equably in the combustion of *nine wax candles*, each ¾ of an inch in diameter, all burning together, or at the same time, with clear bright flames."

The two paragraphs which follow this are especially remarkable, as they show that Rumford distinctly saw the source of this heat in the mechanical energy which was expended during its production:—

"As the machinery used in this experiment could easily be carried round by the force of one horse (though, to render the work lighter, two horses were actually employed in doing it), these computations show further how large a quantity of heat might be produced, by proper mechanical contrivance, merely by the strength of a horse, without fire, light, combustion, or chemical decomposition; and, in case of necessity, the heat thus produced might be used in cooking victuals.

"But no circumstances can be imagined, in which this method of procuring heat would not be disadvantageous; for more heat might be obtained by using the fodder, necessary for the support of a horse, as fuel."

After bringing forward arguments and direct experiments to prove that the evolution of heat cannot have been due to an alteration in the capacity for heat of the particles of metal detached from the larger solid masses by the friction, and that it cannot have been furnished by the air, nor by the water, nor by the pieces of metal by which the cylinder and borer were supported, he says:—"It appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated, in the manner the heat was excited and communicated in these experiments, except it be MOTION."

According to Joule's reduction of these results, they indicate that the heat required to raise the temperature of a pound of water one degree Fahr., is equivalent to the mechanical energy represented by 1034 foot-pounds. This number differs considerably from that deduced from the more accurate experiments to be described below; but the difference is of the kind that might have been anticipated, and, considering the manner in which Rumford's experiments were made, it is not excessive. It will be seen that these were not of a kind to furnish accurate data for determining the quantitative relation between heat and work, and it even seems likely that the idea of instituting a comparison between these two quantities first occurred to Rumford after the experiments were finished, his idea, during their performance, having been rather *qualitative* than quantitative, and his primary object, as indicated in the title of his paper, to ascertain the nature of the source of the heat developed by friction. But, although the numerical results of this investigation were not sufficiently definite to possess any great value, the investigation, as a whole, is of great importance as indicating a distinct stage in the development of ideas concerning the nature of heat and its relations to other forms of energy; and it is for this reason that we have devoted to it so comparatively large a share of space.

These ideas seem to have advanced but little beyond this point until about the year 1842. In that year J. R. Mayer introduced into science the expression "mechanical equivalent of heat" (Ann. Ch. Pharm. xlii. 233; Phil. Mag. [4] xxiv. 371), and thereby—probably as much as by the calculation of the numerical value of this equivalent, founded upon the then inaccurately known ratio of the two specific heats of air—contributed to promote the general adoption of the view that heat and work are mutually convertible. In the same year, Colding, of Copenhagen, communicated to the Royal Society of Denmark experiments on the production of heat by friction, from which he concluded that the evolution of heat was proportional to the mechanical energy expended, and independent of the nature of the substances between which the friction took place. But it was Joule who was the first to publish experiments which were at the same time sufficiently varied and sufficiently accurate to attract the general attention of scientific men, and to be accepted by them as definite proof that the transformation of mechanical energy into heat, or of heat into mechanical energy, takes place in every case according to a constant numerical ratio.

Joule's first experiments, bearing directly upon the subject, were published in 1843 (Phil. Mag. [3] xxiii. 441). In this investigation he showed that the heat evolved by the electric current, furnished by a magneto-electric machine, is proportional to the mechanical energy expended; and that the work done by an electro-magnetic engine is derived from the work of chemical affinity in the battery, work which would otherwise be evolved in the form of heat. From these facts he drew the conclusion, "That the quantity of heat capable of increasing the temperature of a lb. of water by one degree of Fahrenheit's scale, is equal to, and may be converted into, a mechanical force capable of raising 838 lb. to the perpendicular height of one foot." In a subsequent paper, read before the Royal Society in 1844 (Phil. Mag. [3] xxvi. 375, 379), he showed that the heat absorbed and evolved by the rarefaction and condensation of air is proportional to the amount of mechanical energy evolved and absorbed in those operations, and obtained a numerical result closely agreeing with that of the electro-magnetic experiments just referred to. In 1845 and 1847 (*ibid.* xxvii. 205; and xxxi. 173) he determined the heat evolved by the friction of water, sperm-oil, and mercury, and obtained the numbers 781·5, 782·1, and 787·6, by experiments on these liquids respectively, as representing the number of foot-pounds which is equivalent to the heat required to raise the temperature of 1 lb. of water 1° Fahrenheit.

Still more elaborate and careful experiments were made by Joule, in 1849 (Phil. Trans. 1850, p. 61; Chem. Soc. Qu. J. iii. 316), upon the friction of water, mercury, and cast-iron, by a method similar to that adopted in those last mentioned. The apparatus employed in this investigation, for the experiments upon water, consisted of a brass paddle-wheel furnished with eight sets of revolving vanes, working between four sets of stationary vanes. This revolving apparatus, of which *fig.* 549 shows a vertical, and *fig.* 550 a horizontal section, was firmly fitted into a copper vessel (see *fig.* 551) containing water, in the lid of which were two necks, one for the axis to revolve in without touching, the other for the insertion of a thermometer. A similar apparatus, but made of iron, and of smaller size, having six rotatory and eight sets of stationary vanes, was used for the experiments on the friction of mercury. The apparatus for the friction of cast-iron consisted of a vertical axis, carrying a bevelled cast-iron wheel, against which a bevelled wheel was pressed by a lever. The wheels were enclosed in a cast-iron vessel filled with mercury, the axis passing through the lid. In each apparatus motion was given to the axis by the descent of leaden weights *w* (*fig.* 551) suspended by strings from the axes of two wooden pulleys, one of which is shown at *p*, their axes being supported on friction-wheels *d d*, and the pulleys were connected by fine twine with a wooden roller *r*, which, by means of a pin, could be easily attached to or removed from the friction apparatus.

Fig. 549.

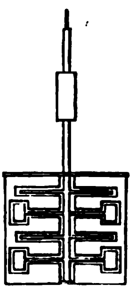


Fig. 550.

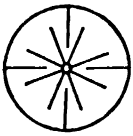
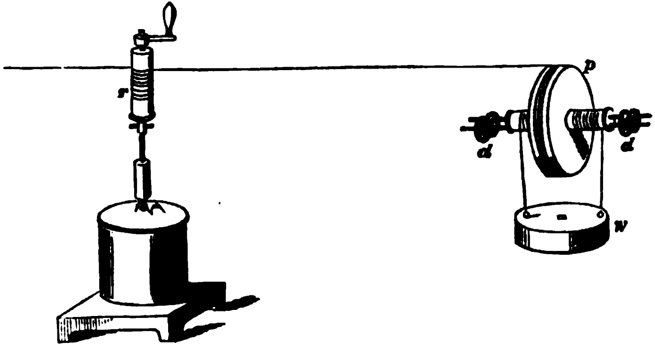


Fig. 551.



The mode of experimenting was as follows: The temperature of the frictional apparatus having been ascertained; and the weights wound up, the roller was fixed to the axis, and the precise height of the weights ascertained; the roller was then set at liberty, and allowed to revolve till the weights touched the floor. The roller was then detached, the weights wound up again, and the friction renewed. This having been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the apartment was ascertained by observations made at the beginning, middle, and end of each experiment. Corrections were made for the effects of radiation and conduction; and, in the experiments with water, for the quantities of heat absorbed by the copper vessel and the paddle-wheel. In the experiments with mercury and cast-iron, the heat-capacity of the entire apparatus was ascertained by observing the heating effect which it produced on a known quantity of water in which it was immersed. In all the experiments, corrections were also made for the velocity with which the weights came to the ground, and for the friction and rigidity of the strings. The thermometers used were capable of indicating a variation of temperature as small as $\frac{1}{500}$ of a degree Fahrenheit.

The following table contains a summary of the results obtained by this method; the second column gives the results as they were obtained in air; the third column, the same results corrected for a vacuum.

Material employed.	Equivalent in air.	Equivalent in vacuo.	Mean.
Water . . .	773·640	772·692	772·692
Mercury . . .	773·762 776·303	772·814 775·352	774·083
Cast-iron . . .	776·997 774·880	776·045 774·930	774·987

In the experiments with cast-iron, the friction of the wheels produced a considerable vibration of the frame-work of the apparatus, and a loud sound; it was therefore necessary to make allowance for the quantity of force expended in producing these effects. The number 772·692, obtained by the friction of water, is regarded as the most trustworthy; but even this may be a little too high; because even in the friction of fluids it is impossible entirely to avoid vibration and sound. The conclusions deduced from these experiments are:

1. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the force expended.*

2. *That the quantity of heat capable of increasing the temperature of* 1 *lb. of water (weighed in vacuo, and between* 55° *and* 60° F.) *by* 1° *F., requires for its evolution the expenditure of a mechanical force represented by the fall of* 772 *lbs. through the space of* 1 *foot.*

Or, the heat capable of increasing the temperature of 1 *gramme of water by* 1° *C., is equivalent to a force represented by the fall of* 423·55 *grammes through the space of* 1 *metre. This is consequently the equivalent of " a unit of heat."*

Since, in consequence of the researches that have been mentioned, the attention of scientific men has been prominently called to the mutual equivalence of heat and work, several investigations have been made, either for the express purpose of ascertaining the numerical ratio expressing that equivalence, or involving determinations from which that ratio can be calculated. In the following table, taken from Verdet's *Exposé de la Théorie Mécanique de la Chaleur* (Paris, 1863), the most trustworthy determinations of the mechanical equivalent of heat are put together. The numbers here given represent the number of kilogramme-metres which is equivalent to 1 kilogramme-degree centigrade, or the number of gramme-metres which is equivalent to 1 gramme-degree.

Table of determinations of the Mechanical Equivalent of Heat.

Nature of the phenomenon whence the determination is drawn.	Philosophers who have indicated the theoretical principle of the determination.	Philosophers who have supplied the experimental data.	Mechanical equivalent.
General properties of air . .	Mayer. Clausius.	V. Regnault. Moll and van Beek.	426
Friction	Joule.	Joule. Favre.	424 413
Work done by the steam-engine	Clausius.	Hirn.	413
Heat evolved by induced currents	Joule.	Joule.	452
Heat evolved by an electro-magnetic engine, at rest and in motion . . .	Favre.	Favre.	443
Total heat evolved in the circuit of a Daniell's battery	Bosscha.	W. Weber. Joule.	420
Heat evolved in a metallic wire through which an electric current is passing .	Clausius.	Quintus Icilius.	400

Dynamical Theory of Heat.

For very long, two rival theories have been held regarding the nature of heat: on the one hand, heat has been viewed as having a material existence, though differing from ordinary matter in being without weight, and in other respects; on the other hand, it has been regarded as a state or condition of ordinary matter, and generally as a condition of motion. From the latter part of the last century, until the modern researches upon the mechanical equivalent, the former view had by far the greater number of adherents. Its popularity may be traced chiefly to the teaching of **Black** and **Lavoisier**. By the former of these philosophers, the various capacities for heat, or specific heats, of different bodies, seem to have been regarded as analogous to the various proportions of the same acid required to neutralise equal quantities of different bases; while the solid, liquid, and gaseous states were explained by him as representing so many distinct proportions in which heat was capable of combining with ordinary matter. Very similar views were advocated by **Lavoisier**: he regarded all gases as compounds of a base characteristic of each, with *caloric*, and supposed that when, as the result of chemical action, they assumed the liquid or solid state, this caloric was set free and appeared as sensible heat. Caloric was thus the physical representative of phlogiston, in the same way as oxygen was its chemical representative: the physical portion of the phenomena previously attributed to dephlogistication, being regarded by Lavoisier as caused by the liberation of caloric, just as the chemical portion was explained by him as combination with oxygen. Thus he uniformly speaks (*Traité élémentaire de Chimie*) of the "decomposition" of oxygen-gas by combustible substances, into oxygen (which combines with the combustible) and caloric (which is set free). It is true that Lavoisier guards himself against definitely expressing his belief in the existence of caloric as a substance, but he enumerates it in his list of elements, and seeks to explain all calorimetric phenomena by the analogy of the combination or separation of elementary bodies. Hence, whether regarded by him as necessarily material or not, it became, for his followers, "an imponderable element."

It will be seen that heat was compared to a material substance, by both Black and Lavoisier, in order to explain its then known quantitative relations; and from this point of view, the conception introduced by them had the great advantage of being more easily grasped than any which the advocates of the immaterial nature of heat had to offer in its place. It was much easier to conceive of definite quantities of an exceedingly subtile substance or fluid, than of definite quantities of motion which was itself undefined as to its nature. It was a direct consequence of the material view, that heat should be considered as indestructible and as incapable of being produced, and therefore that the total quantity of heat in the universe should be regarded as at all times the same.

The greatest difficulty which the upholders of the substantial existence of heat had to meet, was its production by mechanical means, a phenomenon of which, as we have seen, several instances were distinctly recognised. Here it was not easy to deny the actual generation of heat, and to explain the effects as depending merely on its altered distribution. Nevertheless, the evolution of heat by friction and percussion was generally considered, by the advocates of the material view, as in some way resulting from a diminution in the capacities for heat of the bodies operated upon; and this explanation derived considerable support from the remark, made by **Black**, that a piece of soft iron, which has been once made red hot by hammering (see p. 119), cannot be so heated a second time until it has been heated to redness in a fire and allowed to cool. In this case, certainly, it seemed as though the hammering forced out heat from the mass of iron, like water from a sponge, and that a fresh supply was taken up when the iron was put in the fire. But, as has been shown already, this explanation did not satisfy **Rumford**, who, in the investigation described above, made direct experiments upon the specific heat of the chips of metal detached by the friction, and found it to be identical with that of brass under ordinary circumstances. An experiment which proved, if possible, still more decisively, that the heat generated by friction cannot be ascribed to a diminution in the specific heats of the substances, was made by **Davy**, in 1799, the year following the publication of **Rumford's** researches. **Davy** arranged two pieces of ice, so that they could be caused to rub against each other under the exhausted receiver of an air-pump, but so that it was impossible for heat to be imparted to them by conduction, and found that by friction they were rapidly converted into water, that is to say, into a liquid whose specific heat was twice as great as that of ice. From this experiment Davy drew the same conclusion that Rumford had drawn from his own results, and expressed himself in very similar terms:—"The immediate cause of the phenomena of heat then is motion, and the laws of its communication are precisely the same as the laws of the communication of motion." (*Elements of Chemical Philosophy*, London, 1812, pp. 94, 95.) Similar views were very forcibly advocated by Dr. Thomas Young in his *Lectures on Natural Philosophy;* but, by the majority of scientific men, facts such as we have been referring to, though recognised as difficulties in the way of the material theory of heat, were not allowed to cause its rejection. The ease and apparent precision with which the quantitative phenomena of latent and specific heat could be explained, or at least expressed, upon this theory, still caused it to be generally preferred to one which gave a less definite and, as it seemed, more hypothetical explanation of these phenomena. The mechanical, or dynamical theory, which regarded heat as consisting in a state of molecular motion, cannot be said to have been definitely established until it also was made quantitative,—until it was shown that exact numerical laws regulated the production of heat by work or of work by heat, equally with its production during solidification, or disappearance during fusion. This, as we have seen, was effectually accomplished by Joule, and chiefly as the result of his investigations and of others conducted in the same spirit, philosophers have now been compelled to extend their ideas of quantity from matter to energy, and thus has arisen the new science of Energetics, or the quantitative study of the transformations of energy (as chemistry is the quantitative study of the transformation of matter), comprehending and uniting all the different branches of physical science.

We cannot attempt to give anything like an adequate idea of the state of development which the mechanical theory of heat has now reached; but, in order to illustrate the general nature of the theory, and to show in what sort of way the conception that "heat is motion" has been applied to the explanation of such phenomena as have formed the subject of this article, we give here an outline of the view of the constitution of gases which this theory affords, first put forward, in its present form, by Joule (see Ann. Ch. Phys. [3] l. 381) and subsequently developed by Krönig (Pogg. Ann. xcix. 315) and Clausius (*ibid.* 353), and of the explanation of the relations existing between solids, liquids, and gases, which has been deduced from it by the last-named philosopher. The account which follows, of these applications of the dynamical theory, is taken from Watts's Supplement to *Graham's Elements of Chemistry.* It will be seen that the explanations of phenomena which this theory affords, are at least equally definite with those which can be given upon the view of the material nature of heat.

First, then, it is assumed that the particles of all bodies are in constant motion, and that this motion constitutes heat, the kind and quantity of motion varying according to the state of the body, whether solid, liquid, or gaseous.

In gases, the molecules—each molecule being an aggregate of atoms—are supposed to be constantly moving forward in straight lines, and with a constant velocity, till they impinge against each other or against an impenetrable wall. This constant impact of the molecules produces the expansive tendency or elasticity, which is the peculiar characteristic of the gaseous state. The rectilinear movement is not, however, the only one with which the particles are affected. For the impact of two molecules, unless it takes place exactly in the line joining their centres of gravity, must give rise to a rotatory motion; and, moreover, the ultimate atoms of which the molecules are composed may be supposed to vibrate within certain limits, being, in fact, thrown into vibration by the impact of the molecules. This vibratory motion is called, by Clausius, *the motion of the constituent atoms* (*Bewegungen der Bestandtheile*). The total quantity of heat in the gas is made up of the progressive motion of the molecules, together with the vibratory and other motions of the constituent atoms; but the progressive motion alone, which is the cause of the expansive tendency, determines the *temperature.* Now, the outward pressure exerted by the gas against the containing envelope arises, according to our hypothesis, from the impact of a great number of gaseous molecules against the sides of the vessel. But at any given temperature, that is, with any given velocity, the number of such impacts taking place in a given time, must vary inversely as the volume of the given quantity of gas; hence *the pressure varies inversely as the volume or directly as the density,* which is Boyle's law.

When the volume of the gas is constant, the pressure resulting from the impact of the molecules is proportional to the sum of the masses of all the molecules multiplied into the squares of their velocities, in other words, to the so-called *vis viva* or *living force* of the progressive motion.

If, for example, the velocity be doubled, each molecule will strike the sides of the vessel with a two-fold force; and its number of impacts in a given time will also be doubled; hence the total pressure will be quadrupled.

Now we know that when a given quantity of any perfect gas is maintained at a constant volume, it tends to expand by $\frac{1}{273}$ of its bulk at zero for each degree centigrade. Hence the pressure or elastic force increases proportionally to the temperature reckoned from −273° C.; that is to say, to the absolute temperature. Consequently, the *absolute temperature is proportional to the* vis viva *of the progressive motion.*

Suppose a vessel of the form of a rectangular parallelopiped, the lengths of whose sides are x, y, z, to contain n gas-molecules, each having the mass m. Suppose, also, the space enclosed by this vessel to be divided into $\frac{n}{6}$ equal cubes; and at a given instant let there be in each of these cubes six gas-molecules, moving severally in the directions $+x$, $-x$, $+y$, $-y$, $+z$, $-z$, and with the common velocity c. Let it also be supposed that the molecules exert no mutual action upon each other, but pass without hindrance from side to side of the vessel. It is required to determine the pressure, which the gas exerts against one of the sides, yz, of the vessel. The pressure arising from the impact of a single gas-molecule is mca, if a denote the number of impacts which take place in a unit of time. Now, a molecule moving at right angles to yz, or parallel to x, strikes against yz every time that it passes over the space $2x$; therefore $a = \frac{c}{2x}$.

To find the total pressure P upon yz, the quantity, mca, must be multiplied by the number of molecules which move parallel to x, which number, since two atoms out of every six are parallel to x, is $\frac{n}{3}$. Hence $P = m.c.\frac{c}{2x}\cdot\frac{n}{3}$. And the pressure p upon a unit of surface of the side yz, is $p = m.c.\frac{c}{2x}\cdot\frac{n}{3}\cdot\frac{1}{yz}$; or if we put $xyz = v$, and leave out the constant factor:

$$p = \frac{nmc^2}{v}.$$

This expression shows that the pressure exerted upon a unit of surface is the same for each side of the vessel; also, that the pressure is inversely in proportion to the volume of the gas, which is Boyle's law.

The product, mc^2, or the *vis viva* of an atom, is the expression of the temperature reckoned from the absolute zero, or —273° C.

If, in the preceding value of p, we put $mc^2 = \tau$, we have

$$p = \frac{n\tau}{v},$$

that is to say, when the volume is constant, the pressure varies directly as the absolute temperature. (Krönig.)

If, for two different gases, we suppose p, τ and v, equal, it follows from this expression, that n also must be the same for both. That is to say, at the same temperature and pressure, equal volumes of different gases contain the same number of molecules. Hence also, the mass, m, of a molecule is proportional to the specific gravity, s, of the gas: or, the molecular weights of different substances are proportional to their vapour-densities (taken at temperatures at which the vapours have the properties of true gases).

Clausius, taking into consideration the *vis viva* of the vibratory and rotatory movements as well of the progressive movements, arrives at the expression, $p = \frac{nmc^2}{3v}$, or $pv = \frac{nmc^2}{3}$, which differs from that of Krönig only by a constant factor.

From this equation, it is possible to deduce the mean value of the absolute progressive velocity of the molecules of any gas for any given temperature. It gives, in fact, directly,

$$c^2 = \frac{3pv}{nm},$$

or, putting q for the weight of the gas, and g for the force of gravity,—

$$c^2 = \frac{3gpv}{q},$$

an expression which contains only numerically determinable quantities. Denoting by ρ the density of the gas compared with that of air at 0°, introducing into the formula the known values of the weight of a litre of air and of the force of gravity, taking p equal to the normal atmospheric pressure, and denoting the absolute temperature by τ, the value of c, expressed in metres, becomes

$$c = 485\sqrt{\frac{\tau}{273\rho}},$$

which gives at 0° C., for Oxygen $c = 461$ metres per second
„ Nitrogen $c = 492$ „ „
„ Hydrogen $c = 1844$ „ „

Hence, the velocity of translation of the molecules of a gas is inversely as the square-root of its density, which gives Graham's law of the diffusion of gases, and the law of their velocity of entrance into a vacuum.

Moreover, as the motions of the constituent particles of a gas depend on the manner in which its atoms are united, it follows that in any given gas the different motions must be to one another in a constant ratio; and, therefore, the *vis viva* of the progressive motion must be an aliquot part of the entire *vis viva* of the gas; hence also the absolute temperature is proportional to the total *vis viva* arising from all the motions of the particles of the gas.

From this it follows that the quantity of heat which must be added to a gas of constant volume in order to raise its temperature by a given amount, is constant and independent of the temperature. In other words, the specific heat of a gas referred to a given volume is constant, a result which agrees with the experiments of Regnault, mentioned at p. 34. This result may be otherwise expressed, as follows: *The total* vis viva *of the gas is to the* vis viva *of the progressive motion of the molecules, which is the measure of the temperature, in a constant ratio.* This ratio is different for different gases, and is greater as the gas is more complex in its constitution; in other words, as its molecules are made up of a greater number of atoms. The specific heat referred to a constant pressure is known to differ from the true specific heat only by a constant quantity (see p. 42).

The relations just considered between the pressure, volume and temperature of gases, presuppose, however, contain conditions of molecular constitution, which are, perhaps, never rigidly fulfilled; and accordingly, the experiments of Magnus and Regnault (p. 48) show that gases do exhibit slight deviations from Gay-Lussac and Boyle's laws. What the conditions are which strict adherence to these laws would require, will be better understood by considering the differences of molecular constitution which must exist in the solid, liquid, and gaseous states.

A movement of molecules must be supposed to exist in all three states. In the *solid state*, the motion is such that the molecules oscillate about certain positions of equilibrium, which they do not quit, unless they are acted upon by external forces. This vibratory motion may, however, be of a very complicated character. The constituent atoms of a molecule may vibrate separately; the entire molecules may also vibrate as such about their centres of gravity, and the vibrations may be either rectilinear or rotatory. Moreover, when extraneous forces act upon the body, as in shocks, the molecules may permanently alter their relative positions.

In the *liquid state*, the molecules have no determinate positions of equilibrium. They may rotate completely about their centres of gravity, and may also move forward into other positions. But the repulsive action arising from the motion is not strong enough to overcome the mutual attraction of the molecules and separate them completely from each other. A molecule is not permanently associated with its neighbours, as in the solid state; it does not leave them spontaneously, but only under the influence of forces exerted upon it by other molecules, with which it then comes into the same relation as with the former. There exists, therefore, in the liquid state, a vibratory, rotatory and progressive movement of the molecules, but so regulated, that they are not thereby forced asunder, but remain within a certain volume without exerting any outward pressure.

In the *gaseous* state, on the other hand, the molecules are removed quite beyond the sphere of their mutual attractions, and travel onward in straight lines according to the ordinary laws of motion. When two such molecules meet, they fly apart from each other, for the most part, with a velocity equal to that with which they came together. The perfection of the gaseous state, however, implies: 1. That the space actually occupied by the molecules of the gas be infinitely small in comparison with the entire volume of the gas.—2. That the time occupied in the impact of a molecule, either against another molecule or against the sides of the vessel, be infinitely small in comparison with the interval between any two impacts.—3. That the influence of the molecular forces be infinitely small. When these conditions are not completely fulfilled, the gas partakes more or less of the nature of a liquid, and exhibits certain deviations from Gay-Lussac and Boyle's laws. Such is, indeed, the case with all known gases; to a very slight extent with those which have not yet been reduced into the liquid state; but to a greater extent with vapours and condensable gases, especially near the points of condensation.

Let us now return to the consideration of the liquid state. It has been said that the molecule of a liquid, when it leaves those with which it is associated, ultimately takes up a similar position with regard to other molecules. This, however, does not preclude the existence of considerable irregularities in the actual movements. Now, at the surface of the liquid, it may happen that a particle, by a peculiar combination of the rectilinear, rotatory and vibratory movements, may be projected from the neighbouring molecules with such force as to throw it completely out of their sphere of action, before its projectile velocity can be annihilated by the attractive force which they exert upon it. The molecule will then be driven forward into the space above the liquid, as if it belonged to a gas, and that space, if originally empty, will, in consequence of the action just described, become more and more filled with these projected molecules, which will comport themselves within it exactly like the molecules of a gas, impinging and exerting pressure upon the sides of the envelope. One of these sides, however, is formed by the surface of the liquid, and when a molecule impinges upon this surface, it will, in general, not be driven back, but retained by the attractive forces of the other molecules. A state of equilibrium, not static, but dynamic, will therefore be attained when the number of molecules projected in a given time into the space above, is equal to the number which in the same time impinge upon and are retained by the surface of the liquid. This is the process of vaporisation. The density of the vapour required to ensure the compensation just mentioned, depends upon the rate at which the particles are projected from the surface of the liquid, and this again upon the rapidity of their movement within the liquid, that is to say, upon the temperature. It is clear, therefore, that the density of a saturated vapour must increase with the temperature.

If the space above the liquid is previously filled with a gas, the molecules of this gas will impinge upon the surface of the liquid, and thereby exert pressure upon it; but as these gas-molecules occupy but an extremely small proportion of the space above the liquid, the particles of the liquid will be projected into that space almost as if it were empty. In the middle of the liquid, however, the external pressure of the gas acts in a different manner. There also it may happen that the molecules may be separated with such force as to produce a small vacuum in the midst of the liquid. But this space is surrounded on all sides by masses which afford no passage to the disturbed molecules; and in order that they may increase to a permanent vapour-bubble, the number of molecules projected from the inner surface of the vessel must be such as to produce a pressure outwards, equal to the external pressure tending to compress the vapour-bubble. The boiling point of the liquid will, therefore, be higher as the external pressure is greater.

According to this view of the process of vaporisation, it is possible that vapour may rise from a solid as well as from a liquid; but it by no means necessarily follows that vapour must be formed from all bodies at all temperatures. The force which holds together the molecules of a body may be too great to be overcome by any combination of molecular movements, so long as the temperature does not exceed a certain limit.

The *production* and *consumption of heat* which accompany changes in the state of aggregation, or of the volume of bodies, are easily explained, according to the preceding principles, by taking account of the *work* done by the acting forces. This work is partly external to the body, partly internal. To consider first the internal work:

When the molecules of a body change their relative positions, the change may take place either in accordance with or in opposition to the action of the molecular forces existing within the body. In the former case, the molecules, during the passage from one state to the other, have a certain velocity imparted to them, which is immediately converted into heat; in the latter case, the velocity of their movement, and consequently the temperature of the body, is diminished. In the passage from the solid to the liquid state, the molecules, although not removed from the spheres of their mutual attractions, nevertheless change their relative positions in opposition to the molecular forces, which forces have, therefore, to be overcome. In evaporation, a certain number of the molecules are completely separated from the remainder, which again implies the overcoming of opposing forces. In both cases, therefore, work is done, and a certain portion of the *vis viva* of the molecules, that is, of the heat of the body, is lost. But when once the perfect gaseous state is attained, the molecular forces are completely overcome, and any further expansion may take place without internal work, and, therefore, without loss of heat, provided there is no external resistance.

But in nearly all cases of change of state or volume, there is a certain amount of external resistance to be overcome, and a corresponding loss of heat. When the pressure of a gas, that is to say, the impact of its atoms, is exerted against a movable obstacle, such as a piston, the molecules lose just so much of their moving power as they have imparted to the piston, and, consequently, their velocity is diminished and the temperature lowered. On the contrary, when a gas is compressed by the motion of a piston, its molecules are driven back with greater velocity than that with which they impinged on the piston, and, consequently, the temperature of the gas is raised.

When a liquid is converted into vapour, the molecules have to overcome the atmospheric pressure or other external resistance, and, in consequence of this, together with the internal work already spoken of, a large quantity of heat disappears, or is rendered *latent*, the quantity thus consumed being to a considerable extent affected by the external pressure. The liquefaction of a solid not being attended with much increase of volume, involves but little external work; nevertheless the atmospheric pressure does influence, to a slight amount, both the latent heat of fusion and the melting point.

We must here mention, in conclusion, a very remarkable consequence of the relation of mutual convertibility which, as we have endeavoured to show, exists between heat and other forms of energy. "Professor William Thomson has pointed out the fact, that there exists (at least in the present state of the known world) a predominating tendency to the conversion of all the other forms of physical energy into heat, and to the uniform diffusion of all heat throughout all matter. The form in which we generally find energy originally collected, is that of a store of chemical power, consisting of uncombined elements. The combination of these elements produces energy in the form known by the name of electric currents, part only of which can be employed in analysing compounds, and thus reconverted into a store of chemical power; the remainder is necessarily converted into heat: a part only of this heat can be employed in analysing compounds, or in reproducing electric currents. If the remainder of the heat be employed in expanding an elastic substance, it may be entirely converted into visible motion, or into a store of visible mechanical power (by raising weights, for example), provided the elastic substance is enabled to expand until its temperature falls to the point which corresponds to the absolute privation of heat; but unless this condition be fulfilled, a certain proportion only of the heat, depending upon the range of temperature through which the elastic body works, can be converted, the rest remaining in the state of heat. On the other hand, all visible motion is of necessity ultimately converted entirely into heat by the agency of friction. There is, then, in the present state of the known world, a tendency towards the conversion of all physical energy into the sole form of heat.

"Heat, moreover, tends to diffuse itself uniformly by conduction and radiation, until all matter shall have acquired the same temperature.

"There is, consequently, Professor Thomson concludes, so far as we understand the present condition of the universe, a tendency towards a state in which all physical energy will be in the state of heat, and that heat so diffused that all matter will be at the same temperature; so that there will be an end of all physical phenomena.

"Vast as this speculation may seem, it appears to be soundly based on experimental data, and to represent truly the present condition of the universe, so far as we know it." (Rankine, Phil. Mag. [4] iv. 359.)

⁂ For *Radiation and Conduction of Heat*, see RADIATION.

APPENDIX.

The following table gives the temperatures measured by the air-thermometer, at which, according to Regnault's experiments (Mém. Acad. Sciences, xxvi. 658), the vapours of the liquids enumerated in it exert a pressure equal to that of 760 millimetres of mercury:—

Substance.	Temperature	Substance.	Temperature.
Nitrous oxide	− 87·90°	Chloride of silicon	56·81°
Carbonic anhydride	− 78·2	Chloroform	60·16
Sulphydric acid	− 61·8	Methylic alcohol	66·78
Ammonia	− 38·5	Trichloride of phosphorus	73·80
Chlorine	− 33·6	Perchloride of carbon (CCl^4)	76·50
Chloride of methyl	− 23·73	Alcohol	78·26
Oxide of methyl	− 23·65	Benzene	80·36
Sulphurous anhydride	− 10·08	Bromide of ethylene	131·60
Chloride of ethyl	+ 12·50	Oil of turpentine	159·15
Chloride of cyanogen	12·66	Oxalate of methyl	164·20
Chloride of boron	18·23	Oil of lemons	174·80
Ether	34·97	Mercury	357·25
Bromide of ethyl	38·37	Sulphur	448·00
Sulphide of carbon	46·20		

The next table, also from Regnault's experiments (*Op. cit.* pp. 327–332), gives the specific heats of various substances in different states of aggregation. Where, in the column indicating the temperature, some particular degree is given, the number representing the specific heat is the *elementary* specific heat at that degree of temperature,—that is, the quantity of heat required to cause a *very small* alteration of temperature in one gramme of the substance, compared with the quantity required to cause a like infinitesimal alteration of temperature in 1 gramme of water. When an interval of temperature is given, the specific heat is the mean specific heat within that interval:—

Substance.	Solid.		Liquid.		Gaseous.	
	Temperature.	Specific Heat.	Temperature.	Specific Heat.	Temperature.	Specific Heat.
Water .	– 78° to 0°	0·474	10°	1·0	128° to 220°	0·4805
,, .	– 20 to 0	0·504	10 to 100	1·0		
Bromine	– 77·8 to – 25	0·0833	– 7·3 to 10	0·1060	83 to 228	·0555
,			+ 13 to 58	·1129		
Alcohol			– 20	·5053	105 to 220	·4534
,,			0	·5475		
,,			+ 20	·5951		
,,			40	·6479		
,,			60	·7060		
,,			80	·7694		
Ether .			– 30	·5113	70 to 220	·4797
,,			0	·5290		
,,			+ 30	·5467		
,,			35	·5497		
Sulphide of carbon			– 30	·2303	73 to 192	·1570
,, ,,			0	·2352		
,, ,,			+ 30	·2401		
,, ,,			45	·2426		
Methylic alcohol			0 to 20	·6700	101 to 223	·4580
Acetone			– 30	·4824	129 to 233	·4125
,,			0	·5064		
,,			+ 30	·5302		
,,			60	·5540		
Sulphydrate of ethyl			20 to 70	·4785	120 to 223	·4008
Chloride of ethyl			– 27·6 to + 4·5	·4276	19 to 172	·2738
Bromide of ethyl			0 to 20	·2160	77·7 to 196·5	·1896
Cyanide of ethyl			– 30	·4325	114 to 221	·4262
,, ,,			0	·5086		
,, ,,			+ 30	·5847		
,, ,,			60	·6608		
,, ,,			90	·7369		
Acetate of ethyl .			– 30	·4960	115 to 219	·4008
,, ,,			0	·5274		
,, ,,			+ 30	·5588		
,, ,,			60	·5902		
Chloroform			– 30	·2293	117 to 228	·1567
,,			0	·2324		
,,			+ 30	·2354		
,,			60	·2384		
Chloride of ethylene .			– 30	·2790	111 to 221	·2293
,, ,,			0	·2922		
,, ,,			+ 30	·3054		
,, ,,			60	·3186		
Benzene			20 to 71	·4360	116 to 218	·3754
Oil of turpentine			0	·4106	179 to 249	·5061
,, ,,			40	·4538		
,, ,,			80	·4842		
,, ,,			120	·5019		
,, ,,			160	·5068		
Chloride of silicon			0 to 20	·1900	90 to 234	·1322
Trichloride of phosphorus .			12 to 98	·2092	12 to 246	·1347
Chloride of arsenic			14 to 98	·1760	159 to 268	·1122
Stannic chloride .			14 to 98	·1475	149 to 273	·0939
Tetrachloride of titanium .			12 to 98	·1880	162 to 272	·1290

G. C. F.

HEAVY SPAR. *Barytes. Native Sulphate of Barium.* Ba^2SO^4.—This mineral occurs in crystals belonging to the trimetric system. Ratio of axes *a* : *b* : *c*, 0·6206 : 1 : 0·7618; $\infty P : \infty P$ in the macrodiagonal principal section = 63° 38′; $\infty\breve{P}2 : \infty\breve{P}2$ in the same = 102° 18′; $\breve{P}\infty : \breve{P}\infty$ in the basal section = 74° 36′; $\bar{P}\infty : \bar{P}\infty$ in the same = 100° 40′. *Figs.* 552–556 represent frequently occurring combinations.

Fig. 552.

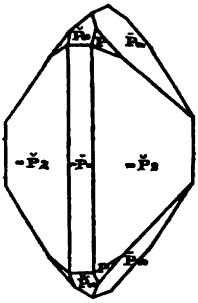


Fig. 553.

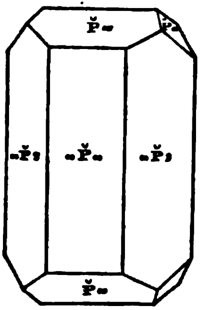


Fig. 554.

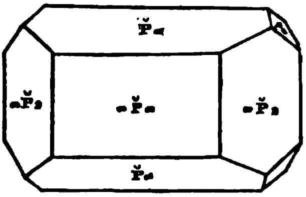


Fig. 555.

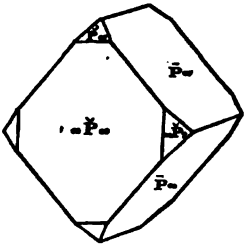
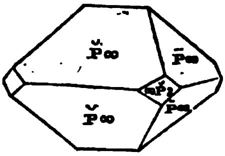


Fig. 556.



The crystals are sometimes prismatically elongated in the direction of one of the axes (*figs.* 553, 554), and sometimes reduced to the tabular form by shortening in one direction (see CRYSTALLOGRAPHY, ii. 149). Cleavage very distinct, parallel to $\infty\breve{P}\infty$. The mineral occurs also massive, with fibrous or laminar structure; also granular. Hardness 2·5 to 3·5. Specific gravity 4·3 to 4·72. Colour white, or inclining to grey, blue, green, yellow, red or brown. Streak white. Lustre splendent, between resinous and pearly. Transparent, exhibiting various degrees of translucency down to perfect opacity. It is sometimes fœtid when rubbed; an impure variety called *hepatite* exhibits this property in a peculiar degree. It decrepitates before the blowpipe, and fuses with difficulty at the edges only. In the inner flame it is reduced to sulphide of barium, and then gives off sulphydric acid when treated with an acid.

Pure heavy spar contains 34·33 per cent. SO^3 and 65·67 Ba^2O; but the mineral generally also contains small quantities of alumina, oxide of iron, silica, and carbonate of calcium. Sulphate of strontium is also a common ingredient. The variety called *calstronbaryte* contains 1 at. lime and 1 at. strontium to 9 at. barium.

It is a very abundant mineral, generally occurring in metalliferous veins, as in the lead-mines of Durham, Cumberland, and Westmoreland. It occurs also in secondary limestones, sometimes in distinct veins, and often in crystals associated with cœlestin and calcspar. In Staffordshire and Derbyshire is found an opaque, massive variety called *cawk*, having an earthy appearance and dirty white colour. On the continent of Europe it is found chiefly at Felsöbanya and Kremnitz, at Freiberg, Marienberg, Clausthal, and Przibram, and at Roya and Roure in Auvergne. Rounded masses, composed of divergent columnar particles, occur at Mount Paterno, near Bologna, hence called *Bolognese stone*. At Freiberg, in Saxony, a variety occurs composed of indistinct prismatic crystals, having a pearly lustre, called *Stangenspath* by Werner. (For the American localities, see Dana, ii. 367.)

Heavy spar occurs altered to calcspar, spathic iron, cerusite, quartz, limonite red iron-ore, pyrites, psilomelane, göthite.

The white varieties of heavy spar are ground and used as a white paint, sometimes alone, but more generally mixed with white lead, the heavy spar alone not possessing sufficient opacity to form a good pigment.

HEBETIN. Anhydrous silicate of zinc. (See WILLEMITE.)

HEDENBERGITE. A black variety of augite, containing a large quantity of iron, little or no magnesia, and no alumina. Specific gravity 3·5. Found chiefly at Tunaberg, in Sweden.

HEDERA HELIX. *Ivy.*—The seeds of this plant contain a nitrogenous substance resembling emulsin, also fat, two peculiar acids, sugar, a small quantity of pectin, and inorganic salts. From the fresh seeds, ether extracts a green oil, containing a solid and a liquid fat. The former is somewhat difficult to saponify, and yields by saponification a fatty acid, which, after repeated crystallisation from alcohol, melts at a temperature not above 30°, and forms a silver salt containing from 27·4 to 27·6 silver (Posselt). The acids contained in ivy-seeds are described in the next article.

HEDERIC ACID. An acid contained, according to Posselt (Ann. Ch. Pharm. lxix. 62) in the seeds of ivy (*Hedera helix*). It is obtained by treating the seeds with ether to remove fatty matters, and boiling the residue with alcohol, which dissolves the acid, and deposits it, after concentration, in needles or delicate scales, colourless, and insoluble in water and in ether. The acid is inodorous, but possesses in a high degree the acrid taste of ivy-seeds. It gives by analysis, 66·5 per cent. C, and 9·5 H; its rational formula is unknown. It gives off 5·42 percent. water at 100°, and chars without melting at a higher temperature. In contact with strong sulphuric acid it assumes a fine purple colour.

Hederic acid decomposes carbonates, and forms gelatinous salts, most of which are insoluble in water, but soluble in alcohol. Even the *potassium-* and *ammonium-*salts dissolve but sparingly in water, and are deposited as gelatinous precipitates when the solutions are left at rest. The *silver-*salt is deposited from boiling alcohol in white crystals.

Ivy-seeds likewise contain another acid, the presence of which greatly impedes the purification of hederic acid. This acid is uncrystallisable; soluble in water, alcohol and ether; forms soluble yellow salts; precipitates lead-salts, reduces nitrate of silver, and colours ferric salts green. It appears to belong to the family of the tannic acids.

HEDERINE. An alkaloïd said to exist in ivy-seeds. (Vandamme and Chevallier, J. Chim. méd. [2] vi. 581.)

HEDYPHANE. A variety of green lead-ore in which the lead is partly replaced by calcium. Found at Långsbanshytta, in Sweden; also called MIMETENE (*q. v.*)

HELENENE. An oily hydrocarbon produced by distilling helenin with phosphoric anhydride. After rectification, it is yellowish, lighter than water, and has a faint odour resembling that of acetone. Boils between 285° and 295°. Gives by analysis 89·0 to 89·8 C, and 10·1 to 10·4 H, agreeing nearly with the formula $C^{19}H^{26}$ (89·8 C, and 10·2 H). Its formation may perhaps be represented by the equation:

$$C^{21}H^{28}O^{3} = C^{19}H^{26} + H^{2}O + 2CO.$$

The evolution of carbonic oxide has not, however, been actually observed.

Helenene heated with fuming sulphuric acid is converted into *sulpho-helenic* acid, the barium-salt of which contains 17·75 per cent. barium.

HELENIN. $C^{21}H^{28}O^{3}$.—A crystalline substance existing in the root of elecampane (*Inula helenium*); it was first observed by Geoffroy, afterwards examined by Dumas, and more especially by Gerhardt (*Traité*, iv. 296). It may be obtained by distilling the root with water, or better by boiling it with alcohol of 80 per cent.; filtering the solution at the boiling heat, and mixing it with three or four times its volume of cold water. The liquid, after twenty-four hours, deposits helenin in long quadrilateral prisms.

Helenin is perfectly colourless, and has very little taste or odour. It is insoluble in water, but very soluble in alcohol and ether. It melts at 72°, and boils between 275° and 280°, decomposing more or less at the same time.

Helenin is not attacked by alkalis in aqueous or alcoholic solution; but when heated with potash-lime, it yields a resinous compound, which remains combined with the potash. Strong sulphuric acid dissolves it with blood-red colour, forming a conjugated acid. Hydrochloric acid gas is absorbed by it in large quantity.

By *chlorine*, with the aid of heat, it is converted into *chlorhelenin*, perhaps $C^{21}H^{24}Cl^{4}O^{3}$; and by nitric acid into *nitrohelenin*. Phosphoric anhydride converts it into *helenene.*

HELIANTHIC ACID. $C^{14}H^{8}O^{7},HO$?—An acid obtained from sunflower seeds, belonging, according to Ludwig and Kromayer, to the tannic acid group. By boiling with moderately dilute hydrochloric acid in a stream of hydrogen, it is resolved into fermentable sugar, and an acid violet colouring matter.

HELIANTHUS ANNUUS. *The Sunflower.*— The peeled seeds of this plant contain, according to **Ludwig** and **Kromayer** (Arch. Pharm. [2] xcix. 1, 285): 1. Helianthic acid.—2. A *fat oil*, amounting to 40 per cent. of the peeled seeds.—3. A small quantity of *fermentable sugar*, uncrystallisable, and capable of reducing cupric oxide, only when the latter is present in considerable quantity in alkaline solution.—4. A substance soluble in alcohol, precipitated from this solution by ether in the form of a syrup, not directly fermentable, and not capable of reducing cupric oxide in alkaline solution, but convertible by boiling, either alone or with acids, into a substance which reduces cupric to cuprous oxide, and perhaps constituting a link between inulin and sugar.—5. *Legumin*.—6. A substance perhaps identical with inulin, insoluble in cold water and alcohol, and converted by boiling with dilute acids into a body which reduces cupric to cuprous oxide.—7. Mulders' horny vegetable albumin (a body resembling cellulose, soluble in strong sulphuric acid, and precipitable from this solution by water).—8. A mixture resembling cerebrin, and another resembling oleophosphoric acid.—9. Cellulose.

The nitrogenous substance, which is soluble in boiling alcohol, and remains as a gelatinous mass when the alcohol is distilled off, appears to be a compound of helianthic acid with a protein-substance, accompanied by a soapy compound.

The peeled seeds dried in the air at mean temperatures yielded 4·2 per cent. ash, of which 3·8 pts. were insoluble, and 0·4 soluble in water.

HELICIN. $C^{13}H^{16}O^7$. (**Piria**, Ann. Ch. Phys. [3] xiv. 287.)—A body produced by the action of very dilute nitric acid upon salicin:

$$\underset{\text{Salicin.}}{C^{13}H^{18}O^7} + O = H^2O + \underset{\text{Helicin.}}{C^{13}H^{16}O^7};$$

also, together with benzoic acid, by boiling benzo-helicin with magnesia (**Piria**, Ann. Ch. Pharm. xcvi. 380). To prepare it, 1 pt. of pulverised salicin is mixed with 10 pts. of nitric acid of 20° Bm. (specific gravity 1·157), and the mixture is left to itself in an open vessel. In about 24 hours the salicin is completely dissolved, especially if the mixture be stirred from time to time, and crystals of helicin collect at the bottom of the vessel. They must be pressed between paper and purified by washing with ether till the ether which runs off no longer reddens ferric salts. Salicin yields about two-thirds of its weight of helicin.

Helicin crystallises in small, white, very slender needles containing ¾ at. water. It is neutral, slightly bitter, sparingly soluble in cold *water*, dissolves very freely in boiling water; it is soluble also in *alcohol*, but is insoluble in *ether*. At 100° C. it gives off its water of crystallisation, amounting to 4·54 per cent. At 175° it melts, and at a higher temperature gives off vapours of hydride of salicyl. Under the influence of *emulsin*, or of dilute *acids* or *alkalis* at the boiling heat, it is resolved into glucose and hydride of salicyl:

$$\underset{\text{Helicin.}}{C^{13}H^{16}O^7} + H^2O = \underset{\text{Glucose.}}{C^6H^{12}O^6} + \underset{\substack{\text{Hydride}\\\text{of salicyl.}}}{C^7H^6O^2}.$$

At ordinary temperatures, the fixed alkalis and alkaline earths merely increase the solubility of helicin in water.

Benzo-helicin. $C^{20}H^{20}O^8 = C^{13}H^{15}(C^7H^5O)O^7$.—This compound, which is related to helicin in the same manner as populin to salicin, is obtained by dissolving benzo-salicin (populin) in 10 or 12 times its weight of nitric acid of specific gravity 1·3. It crystallises in tufts of silky needles, which do not give off any water when heated. It dissolves in boiling *water*; and if the first drops of a solution filtered at the boiling heat crystallise on cooling, the crystallisation extends throughout the entire mass; but on again applying heat, and leaving the solution to cool slowly and quietly, it solidifies to a gelatinous pulp.

Benzo-helicin is not decomposed by emulsin, but *alkalis* and *acids* convert it into benzoic acid, hydride of salicyl, and glucose:

$$\underset{\substack{\text{Benzo-}\\\text{helicin.}}}{C^{20}H^{20}O^8} + 2H^2O = \underset{\substack{\text{Benzoic}\\\text{acid.}}}{C^7H^6O^2} + \underset{\substack{\text{Hydride}\\\text{of salicyl.}}}{C^7H^6O^2} + \underset{\text{Glucose.}}{C^6H^{12}O^6}.$$

By boiling with *magnesia* (or other bases which do not act upon helicin), it is resolved into benzoic acid and helicin.

Bromhelicin, $C^{13}H^{15}BrO^7.H^2O$, is prepared like chlorhelicin, and exhibits similar reactions, but always separates from solution in the gelatinous form, and when dry, forms a dirty white powder without any appearance of crystallisation.

Chlorhelicin, $C^{13}H^{15}ClO^7$, exists in two modifications, which may be distinguished as α and β.

α *Chlorhelicin* is obtained by agitating helicin with water in a vessel filled with chlorine. The product is purified by pressure, washing with cold water, and solution in boiling water, the liquid as it cools either depositing small needles of monohydrated chlorhelicin, $2C^{13}H^{15}ClO^7.H^2O$, or solidifying to an amorphous jelly containing a larger quantity of water.

α Chlorhelicin is inodorous, bitter, nearly insoluble in cold *water*, easily soluble in hot water and in *alcohol*. The crystals contain 3 per cent. water, which is rather more than the amount required by the formula just given (2·76 per cent.), the excess probably arising from admixture of a small quantity of gelatinous α chlorhelicin. When heated to between 120° and 130°, they give off the whole of their water, and the remaining anhydrous α chlorhelicin, when raised to a higher temperature, gives off vapours of hydride of chlorosalicyl. This product is likewise obtained, together with glucose or its products of decomposition, on heating α chlorhelicin with dilute *acids* or *alkalis*, or by treating it with *emulsin:*

$$C^{13}H^{15}ClO^7 + H^2O = C^{13}H^5ClO^2 + C^6H^{12}O^6.$$

β *Chlorhelicin.* When chlorine is passed into an alcoholic solution of helicin, a white granular substance is obtained, which has the composition of α chlorhelicin, but is insoluble in water, nearly insoluble in boiling alcohol, and is not decomposed in the manner just mentioned by acids, alkalis, or emulsin.

HELICOÏDIN. $C^{26}H^{34}O^{14}$ (Piria, Ann. Ch. Phys. [3] xiv. 292).—This substance, which may be regarded as a compound of helicin and salicin ($C^{13}H^{16}O^7 + C^{13}H^{18}O^7$), is obtained by treating salicin with nitric acid still more dilute than that which is used for the preparation of helicin, viz. of 12° Bm. (specific gravity 1·088). It may be purified by washing with cold water and crystallisation from boiling water. It forms needles resembling those of helicin, and containing $\frac{3}{2}$ at. water ($2C^{26}H^{34}O^{14} + 3H^2O$). Under the influence of emulsin it is decomposed similarly to helicin, yielding, however, saligenin in addition to glucose and hydride of salicyl:

$$\underset{\text{Helicoidin.}}{C^{26}H^{34}O^{14}} + 2H^2O = \underset{\text{Glucose.}}{2C^6H^{12}O^6} + \underset{\text{Hydride of salicyl.}}{C^7H^6O^2} + \underset{\text{Saligenin.}}{C^7H^8O^2}.$$

Alkalis and acids act in the same manner, the latter, however, converting the saligenin into saliretin (C^7H^6O) by abstraction of water.

Helicin, salicin, and helicoïdin are related to one another in the same manner as quinone, colourless hydroquinone, and green hydroquinone.

HELIOTROPE or *Bloodstone.* A variety of chalcedony, having a deep green colour with blood-red spots. It is used as a gem.

HELIX POMATIA. The *Garden* or *Vineyard Snail.*—The shell and operculum of this mollusc have been analysed by B. Wicke (Ann. Ch. Pharm. cxxv. 79), with the following results:—

	Ca^2CO^3	Mg^2CO^3	Earthy Phosphates.	Ferric Phosphate.	SiO^2	Organic Substance.		
Shell . .	96·07	0·98	0·85		1·15	0·95	=	100·00
Operculum .	86·75	0·96	5·36	0·16	0·35	6·42	=	100·00

W. Wicke (Ann. Ch. Pharm. lxxxvii. 224) found in the operculum 94·24 per cent. carbonate, and 5·73 per cent. phosphate of calcium, together with traces of ferric oxide and phosphate of magnesium. He supposes that the phosphate of calcium is contained chiefly in the small nodules which cover the surface of the operculum. Joy (*ibid.* xxxii. 365) found in the shell, 98·5 per cent. carbonate of calcium and 1·5 organic matter, but no phosphoric acid, silicic acid, fluorine, magnesia, or alkalis. Gobley (J. Pharm. [3] xxxiii. 161) found that the shell contained 70 per cent. water, and when dried consisted almost wholly of carbonate of calcium, with small quantities of earthy and ferric phosphates, and animal matter.

In the animal itself, Gobley found a peculiar mucus, containing a small quantity of carbonate of potassium, which gives it an alkaline reaction, redissolves in water after drying, but loses this property after a while. Gobley also found, besides the salts usually occurring in the animal organism, a small quantity of chloride of ammonium, a peculiar compound of animal matter with carbonate of calcium, partially soluble in water, and traces of iodine. Beneke (Ann. Ch. Pharm. cxii. 249) found in the animal, a peculiar fatty substance called myelin, existing also in the brain and other organs of the higher animals, which swells up in peculiar forms when soaked in water.

HELLEBORINE. An azotised body contained in the root of black hellebore (*Helleborus hiemalis*). It is obtained by exhausting the root with alcohol, diluting the extract with a certain quantity of water, which precipitates a resin, and concentrating the filtered liquid.

It forms colourless crystals, having a harsh bitter taste, soluble in water and in alcohol, more soluble in ether. The solutions are neutral to test-paper. It is decomposed by heat, also by nitric and sulphuric acids. Heated with potash it gives off ammonia. It is not precipitated from its solutions by acetate of lead, chloride of mercury, or iodide of potassium. (W. Bastick, Pharm. J. Trans. xii. 174.)

HELLEFLINTA. Called also *Leelite.* A variety of felspar, occurring at Gryphyttan, in Sweden, having a peculiar waxy lustre and deep flesh-red colour.

HELLENENE and **HELLENIN.** See HELENENE and HELENIN (p. 138).

HELMINTHE. A variety of chlorite occurring in felspar and quartz. (Dana, ii. 294).

HELMINTHOLITE. A variety of limestone, generally of a dark colour, and distinguished by the beautiful red and green iridescence of the fossil shells which it contains. It is found in Carinthia, at Halle in the Tyrol, and other localities, and is made into a variety of ornamental articles. (Handw. d. Chem. iii. 848.)

HELVIN. *Tetrahedral Garnet.*—A mineral consisting of silicate of manganese, iron, and glucinum, combined with oxysulphide of manganese. It occurs in regular tetrahedrons. Hardness 6 to 6·5, rather greater than that of felspar. Specific gravity 3·1 to 3·3. Lustre vitreous, inclining to resinous. Colour wax-yellow, inclining to yellowish brown and siskin-green. Streak uncoloured. Subtranslucent. Fracture uneven. On charcoal, in the reducing flame, it melts, with intumescence, to a yellow opaque globule. When finely pulverised it is decomposed by hydrochloric acid, with evolution of sulphydric acid and separation of gelatinous silica.

Analyses: 1, 2. From Saxony, by C. Gmelin (Pogg. Ann. iii. 53). 3. From Norway, by Rammelsberg (*Mineralchemie*, p. 700):

	SiO^2	S	Al^4O^3	G^2O	Fe^2O	Mn^2O	Loss by ignition.	
1.	35·27	. .	1·44	8·03	8·00	42·12		
2.	33·26	5·05	12·03		5·56	41·76	1·15	= 98·81
3.	33·13	5·71	. .	11·16	4·00	49·12	. .	= 103·42

Hence Rammelsberg deduces the formula

$$2(Mn\,;\,Fe)^2S\,.\,3[2(Mn\,;\,Fe)^2O.2SiO^2 + 2G^2O.SiO^2]$$

which is reducible to the form of an orthosilicate united with a protosulphide,

$$3M^4SiO^4.2M^2S.$$

Helvin affords the only known example of a native compound of a silicate with a sulphide. It is found in the gneiss of Schwarzenberg, in Saxony, associated with garnet, quartz, flints, and calcspar: at Breitenbrunn, in Saxony; and on the Hortekalie, a mountain in the Liesthal, near Drammen, in Norway.

HEMIBROMHYDRIN. See BROMHYDRINS.

HEMI-COMPOUNDS. Binary compounds containing 1 at. of an electronegative or chlorous radicle, combined with 2 or 4 at. of a monatomic electro-positive or basylous radicle, according as the electro-negative radicale is mono- or di-atomic, *e. g.* hemichloride of copper = Cu^2Cl; hemioxide of copper, Cu^4O ($Cu = 31{\cdot}6$). Such compounds are often called *di-compounds*; but this term is used in this Dictionary in a different sense (ii. 321).

HEMIHEDRY. See CRYSTALLOGRAPHY (ii. 121, 128, 136, 140, 150, 156).

HEMILOGOUS SERIES. A name applied by Schiel (Zeitschr. Ch. Pharm. 1860, p. 44) to series of organic compounds, the terms of which differ from one another by nCH.

HEMIMORPHISM. Hemimorphous crystals, according to most authors, are those which are unsymmetrically terminated at the two ends of the principal axis, *e. g.* siliceous calamine (i. 714), sulphate of magnesium (ii. 150). Laurent, however (Compt. chim. 1849, p. 269), applied the same term to bodies which are similar, or to a certain extent analogous, in composition (*d'une certaine analogie dans leur composition*), and crystallise in forms (belonging to the same or to different systems) in which some of the dihedral angles are nearly equal, while the rest are very unequal.

HEMIMORPHITE. Syn. with SILICEOUS CALAMINE (i. 714).

HEMIPINIC ACID. $C^{10}H^{10}O^6$. (Wöhler [1844], Ann. Ch. Pharm. i. 17.—Blyth, *ibid.* l. 36 and 43.—Anderson, *ibid.* lxxxvi. 194.—Matthiessen and Foster, Proc. Roy. Soc. xi. 58; further, Phil. Trans. 1863; Chem. Soc. J. xv. 346.)—This acid is produced: 1. By the oxidation of opianic acid: $C^{10}H^{10}O^5 + O = C^{10}H^{10}O^6$, which may be effected by the action of peroxide of lead and sulphuric acid (Wöhler), or of aqueous dichloride of platinum (Blyth).—2. By the oxidation of narcotine with dilute nitric acid (Anderson), or with peroxide of lead and sulphuric acid, or peroxide of manganese and hydrochloric acid (Wöhler), or with excess of aqueous dichloride of platinum (Blyth). In these reactions, the narcotine is first converted into opianic acid, which then suffers further decomposition.—3. Together with meconin, by the decomposition of opianic acid under the influence of caustic potash (Matthiessen and Foster):

$$\underset{\text{Opianic acid.}}{2C^{10}H^{10}O^5} = \underset{\text{Meconin.}}{C^{10}H^{10}O^4} + \underset{\text{Hemipinic acid.}}{C^{10}H^{10}O^6}$$

Preparation.—1. Opianic acid is heated to the boiling point with water and peroxide of lead; dilute sulphuric acid is added drop by drop till carbonic acid begins to escape; the liquid is left to cool partially; sulphuric acid is then added by drops till all the lead is precipitated, and the filtrate is evaporated to the crystallising point. The first crystals are sometimes mixed with unaltered opianic acid, but are easily purified from it by their much greater solubility in water (Wöhler).—2. The mother-liquor resulting from the action of dilute nitric acid upon narcotine (*q. v.*), after the separation of meconin, cotarnine and opianic acid, contains hemipinic acid, which may be obtained by precipitating this mother-liquor with acetate of lead, and decomposing the precipitate with sulphydric acid. (Anderson.)

3. Opianic acid is mixed with a large excess of potash-ley; the liquid is evaporated nearly to dryness; and the resulting alkaline mass, consisting of meconin and hemipinate of potassium, is dissolved in a moderate quantity of warm water, and mixed with excess of hydrochloric acid, whereby the meconin is separated as an oil, carrying down with it the greater part of the hemipinic acid. The acidified liquid, when quite cold, is poured off from the solid cake of meconin and hemipinic acid formed at the bottom, and evaporated to a small bulk, so as to separate the greater part of the chloride of potassium; this salt is washed with alcohol; the alcoholic washings are mixed with the concentrated mother-liquor; and the fresh quantity of chloride of potassium thus precipitated is removed by filtration or decantation. The clear liquid is evaporated nearly to dryness over the water-bath; the residue thus obtained is again treated with alcohol to separate the last portions of chloride of potassium; and the alcoholic solution is filtered and evaporated. On dissolving the product of these operations, together with the original precipitate of meconin and hemipinic acid, in boiling water, and rendering the solution slightly alkaline by ammonia, nearly all the meconin crystallises out as the solution cools, while hemipinate of ammonium remains in solution, together with a small quantity of meconin. For complete purification, the solution of the ammonium-salt is precipitated by acetate of lead, and the hemipinate of lead, after thorough washing, is decomposed under water by sulphydric acid (Matthiessen and Foster). This mode of preparation is preferable to the oxidation process; because in the latter it is difficult to arrest the action at the right point, so that there is always a risk, either of leaving opianic acid undecomposed, or of losing a portion of the hemipinic acid by further oxidation. (See below.)

Properties.—Hemipinic acid crystallises in colourless oblique rhombic prisms (Wöhler), or large flat rhombohedrons (Blyth). It has a slightly acid astringent taste, and a strong acid reaction. It dissolves with difficulty in cold *water*, more easily in *alcohol* and in *ether*. The crystals effloresce in the air, and give off 13·73 per cent. (= 2 at.) water at 100° C. At 180° it melts, and solidifies to a crystalline mass on cooling. Heated between two watch-glasses, it sublimes in shining laminæ like benzoic acid.

Decompositions.—Hemipinic acid burns with a bright flame. Heated with *peroxide of lead* and *sulphuric acid*, it appears to be completely resolved into water and carbonic anhydride (Wöhler); distilled with excess of concentrated *hydriodic acid*, it is completely resolved into carbonic anhydride, iodide of methyl, and hypogallic acid (Matthiessen and Foster):

$$\underset{\text{Hemipinic acid.}}{C^{10}H^{10}O^6} + 2HI = \underset{\text{Hypogallic acid.}}{C^7H^6O^4} + \underset{\text{Iodide of methyl.}}{2CH^3I} + CO^2$$

Heated with two or three times its weight of strong *hydrochloric acid*—either in a sealed tube to about 110°, or in an open vessel connected with a condenser, in such a manner that the condensed vapour flows back into the mixture, and with an apparatus for evolving hydrochloric acid gas, so that the liquid can be kept constantly saturated with acid, it is resolved into carbonic anhydride, chloride of methyl, and an acid having the composition $C^8H^8O^4$, homologous, therefore, with hypogallic acid:

$$C^{10}H^{10}O^6 + HCl = CO^2 + CH^3Cl + C^8H^8O^4.$$

This acid (not yet named) crystallises in long transparent prisms, nearly insoluble in cold water, not much more soluble in boiling water, more easily soluble in alcohol and ether. When heated, it begins to sublime without decomposition at about 200° C., and bears a temperature of more than 245° without alteration, but at a still higher temperature it melts, and solidifies to a crystalline mass on cooling. It dissolves in strong sulphuric acid, and crystallises unchanged from a warm saturated solution; a cold solution is not precipitated by water. It gives no coloration with ferric chloride; with nitrate of silver it forms a white precipitate, which blackens on boiling. (Matthiessen and Foster.)

When the mother-liquor from which this acid has crystallised is subjected to the prolonged action of hydrochloric acid, hypogallic acid appears to be formed. (Matthiessen and Foster.)

Hemipinates.—Hemipinic acid is dibasic, its normal salts being represented by the formula $C^{10}H^8M^2O^6$. It is distinguished from opianic acid by forming insoluble salts with *lead*, *silver*, and *iron*. The *ammonium-salt* forms crystals permanent in the air.

The *neutral potassium-salt* is very soluble and difficult to crystallise.

The *acid potassium-salt*, $C^{10}H^9KO^6 . \frac{5}{2}H^2O$, forms large hexagonal tables, easily soluble in water and alcohol, insoluble in ether. It gives off its water at 100°.

Barium-salt.—When a solution of hemipinic acid is neutralised with baryta-water, or when solutions of hemipinate of ammonium and chloride of barium are mixed together, the liquid remains clear for a long while if left to itself; but on boiling it for a short time, small, shining crystalline plates of hemipinate of barium are precipitated, and soon fill the liquid, provided the solutions used were not too dilute. The liquid on cooling redissolves this precipitate, and becomes almost or quite clear; but after standing for a few hours, or for a day or two, it again deposits hemipinate of barium, but this time in feathery tufts of very small silky needles; if the liquid be now again heated, these feathery crystals redissolve, and the crystalline plates again make their appearance. This reaction affords the means of recognising hemipinic acid, even when present in small quantity only. (Matthiessen and Foster.)

Ferric hemipinate is a precipitate of a fine orange-yellow colour (Blyth). The *lead-salt* is a white precipitate insoluble in water, but soluble in aqueous acetate of lead, whence it separates in transparent nodules (Wöhler). The *silver-salt*, $C^{10}H^8Ag^2O^6$, is a white precipitate insoluble in water.

Ethyl-hemipinic acid, $C^{10}H^9(C^2H^5)O^6 . \frac{3}{2}H^2O$, is obtained by passing hydrochloric acid gas into a solution of hemipinic acid in absolute alcohol. It crystallises in bulky needles, which give off their water (9·6 per cent.) at 100°. It has a strong acid reaction, is very slightly soluble in cold water, rather more in boiling water. The aqueous solution precipitates ferric salts, but not lead- or silver-salts. The ethylhemipinates are difficult to purify. The *barium-salt* forms needles grouped in tufts. (Anderson.)

HEPATIN. Syn. with GLYCOGEN (ii. 906).

HEPATITE. A variety of heavy spar containing bituminous matter, and distinguished by the hepatic odour which it emits when rubbed or struck.

HEPTYL. C^7H^{15}. *Oenanthyl.*—The radicle, not yet isolated, of heptylic or œnanthylic alcohol and its derivatives.

HEPTYL, ACETATE OF. $C^9H^{18}O^2 = \left.\begin{matrix}C^2H^3O\\C^7H^{15}\end{matrix}\right\}O$. (Bouis and Carlet, Compt. rend. lv. 140; Ann. Ch. Pharm. cxxiv. 353.—Schorlemmer, Chem. Soc. J. xvi. 217).—This compound is obtained:—1. By heating œnanthol (heptylic aldehyde, $C^7H^{14}O$) with zinc and glacial acetic acid. The nascent hydrogen thereby liberated unites with the œnanthol, forming heptylic alcohol; and this, with the excess of acetic acid forms acetate of heptyl. On washing the product with water, and agitating it with acid sulphite of sodium, to remove undecomposed œnanthol, the acetate of heptyl is obtained as an oil floating on the surface (Bouis and Carlet).—2. By decomposing chloride of heptyl with acetate of potassium. The two substances, mixed with glacial acetic acid, are heated in sealed tubes to 150°—160° C., for twelve hours. The products of the reaction are chloride of potassium, acetate of heptyl, and heptylene. On diluting the contents of the tubes with water, drying the light oily liquid which separates with chloride of calcium, and subjecting it to fractional distillation, the heptylene, which boils at 95°, is easily separated from the acetate of heptyl, the boiling point of which is much higher (Schorlemmer). Alcohol may be used in the preparation instead of glacial acetic acid, but it is less convenient, as the last portions of the chloride are then very slow to decompose, requiring a heat of 200° continued for several days. (Schorlemmer.)

Acetate of heptyl is a colourless oily liquid, lighter than water, having an agreeable fruity odour, and boiling at 180° (Bouis and Carlet), between 179° and 181° (Schorlemmer), which is about 10° higher than it should be according to Kopp's law (p. 90). It contains, according to the mean of Schorlemmer's analyses, 68·18 per cent. carbon, and 11·54 hydrogen, the formula requiring 68·35 carbon and 11·39 hydrogen.—By distillation with potash-ley, it yields acetate of potassium and heptylic alcohol.

HEPTYL, BROMIDE OF. This compound is slowly produced, with evolution of hydrobromic acid, when bromine is added to hydride of heptyl, and the mixture is either exposed to sunshine or heated in sealed tubes to 100°; the action may be quickened by adding a little iodine. On distilling the product, a large quantity of undecomposed hydride passes over first, and, as soon as the temperature rises to 110°, the residue begins to decompose and blacken. (Schorlemmer, *loc. cit.*)

HEPTYL, CHLORIDE OF. $C^7H^{15}Cl$. (Petersen, Ann. Ch. Pharm. cxviii. 74.—Schorlemmer, Chem. Soc. J. xv. 423; xvi. 217, 426).—Obtained:—1. By the action of pentachloride of phosphorus on heptylic alcohol, and purified by washing and distillation in the usual way (Petersen).—2. By the action of chlorine, or better of chloride of iodine, on hydride of heptyl. Chlorine gas is passed, not in excess, into a solution of iodine in hydride of heptyl; the unattacked portion of the hydride is then distilled off, and the chloride of heptyl is separated by fractional distillation from the portion boiling between 140° and 160° (Schorlemmer).—3. In like manner, from ethyl-amyl ($C^2H^5.C^5H^{11}$), which is isomeric with hydride of heptyl. The product yields, by fractional distillation, two liquids of constant boiling point, *viz.*, chloride of heptyl, and monochlorinated chloride of heptyl, which are easily separated by distillation, as their boiling points differ by 40°. (Schorlemmer, Chem. Soc. J. xvi. 426.)

Chloride of heptyl is a colourless liquid, having an agreeable fruity odour, and burning with a smoky green-bordered flame. Specific gravity 0·891 at 19°. (Schorlemmer); 0·9983 at 55° (Petersen). Boiling point of the chloride obtained from castor-oil alcohol = 175° (Petersen); of that obtained from hydride of heptyl or from ethyl-amyl = 150° (Schorlemmer). This difference seems to point to the existence of two isomeric modifications of chloride of heptyl. Neither boiling point agrees very well with that calculated according to Kopp's law (p. 91): for the average difference for homologous chlorides of the alcohol-radicles, C^nH^{2n+1}, is about 30°, chloride of ethyl boiling at 11°, and chloride of amyl at 101°: hence chloride of heptyl should boil at about 161°.

Chloride of heptyl contains, according to Petersen's analyses, from 61·68 to 62·25 per cent. carbon, 11·01 to 11·28 hydrogen, and 26·46 chlorine, the formula requiring 62 45 C, 11·16 H, and 26·36 Cl. It is insoluble in *water*, but dissolves easily in *alcohol* and *ether*. Heated in a sealed tube with *acetate of potassium* and alcohol or glacial acetic acid, it yields acetate of heptyl (p. 141); and when heated in like manner with alcoholic *sulphydrate of potassium*, it yields sulphydrate of heptyl. It is scarcely acted upon by strong *potash-ley*, even when heated with it in sealed tubes to 180° for several days, only a small quantity of heptylene being formed, and not a trace of heptylic alcohol. (Schorlemmer.)

Monochlorinated Chloride of Heptyl, $C^7H^{14}Cl.Cl$, isomeric, if not identical, with chloride of heptylene, $C^7H^{14}Cl^2$, is obtained, together with chloride of heptyl, by the action of chloride of iodine on ethyl-amyl (see above). It boils at 190°, and gives by analysis 41·85 per cent. chlorine, the formula requiring 42·01. (Schorlemmer.)

HEPTYL, HYDRATE OF. $C^7H^{16}O = \left.\begin{matrix}C^7H^{15}\\H\end{matrix}\right\}O$. *Heptylic* or *Oenanthylic alcohol.*—This alcohol occurs, together with others, in the fusel-oil from the brandy distilled from marc of grapes (*Weintreber-fuselöl*). The portion of this liquid boiling above 133° C. contains several alcohols of the series $C^nH^{2n+2}O$, higher than amylic alcohol; and by subjecting it to repeated fractional distillation, a portion may be obtained which boils between 155° and 160°, and exhibits the composition and reactions of heptylic alcohol. (Faget, Bull. Soc. Chim. de Paris, 1862, p. 59; Ann. Ch. Pharm. cxxiv. 355.)

Heptylic alcohol is likewise obtained:—1. By the action of nascent hydrogen on œnanthol, $C^7H^{14}O$ (Bouis and Carlet). The œnanthol is treated with zinc and glacial acetic acid, as already described (p. 143), and the resulting acetate of heptyl, distilled with potash, yields the alcohol.—2. From hydride of heptyl, that compound being first converted into chloride, the chloride into acetate, and the acetate into the alcohol by distillation with potash. (Schorlemmer.)

3. By distilling ricinoleate of potassium or sodium with excess of the caustic alkali (i. 98). When castor-oil is saponified with potash and the resulting soap (ricinoleate of potassium) is distilled with excess of solid potash, hydrogen is evolved, and an oily liquid passes over, containing an alcohol, or perhaps two, homologous with ethylic alcohol, together with an aldehyde or an acetone, while sebate of potassium remains in the retort. Bouis, who first observed this reaction, originally regarded the volatile oily product as octylic or caprylic alcohol (Compt. rend. xxxiii. 144; Ann. Ch. Pharm. lxxx. 304). Soon afterwards (Institut, 1851, p. 258; Ann. Ch. Pharm. lxxx. 306) he pronounced it to be heptylic alcohol; but ultimately (Compt.

rend. xxxviii. 935; xli. 603; Ann. Ch. Pharm. xcii. 395; xcvii. 34; in detail, Ann. Ch. Phys. [3] xliv. 77; xlviii. 99), after having succeeded in purifying the alcohol more completely than before, he returned to his first opinion, which was corroborated by the analysis of several derivatives of the alcohol by himself, and also by **Moschnin** (Ann. Ch. Pharm. lxxxvii. 111), **Squire** (Chem. Soc. Qu. J. vii. 108), and **Cahours** (Ann. Ch. Pharm. xcii. 399).—On the other hand, **Railton** (Chem. Soc. Qu. J. vi. 205), from a determination of the vapour-density, and **Wills** (*ibid.* 307), from an analysis of the alcohol, and from the examination of some of its compound ethers, concluded that it is heptylic alcohol. Somewhat later, **Limpricht** (Ann. Ch. Pharm. xciii. 242) showed that the oily distillate obtained as above contains a considerable quantity of a liquid which forms a crystalline compound with acid sulphite of sodium; and by distilling this compound with excess of caustic alkali, he obtained a liquid having the composition of octylic or caprylic aldehyde, $C^8H^{16}O$, which he accordingly regarded as the chief product of the distillation of ricinoleic acid with excess of potash. According to **Städeler**, however (J. pr. Chem. lxii. 241; Jahresber. 1857, p. 361), the compound $C^8H^{16}O$ is not caprylic aldehyde, but the isomeric compound, methyl-œnanthyl, $CH^3.C^7H^{13}O$, belonging to the class of acetones (i. 31), and its formation takes place simultaneously with that of heptylic alcohol, in the manner shown by the equations:

$$\underset{\substack{\text{Ricinoleic}\\\text{acid.}}}{C^{18}H^{34}O^3} + 2KHO = \underset{\substack{\text{Methyl-}\\\text{œnanthyl.}}}{CH^3.C^7H^{13}O} + \underset{\substack{\text{Sebate of}\\\text{potassium.}}}{C^{10}H^{16}K^2O^4} + 2H^2$$

$$\underset{\substack{\text{Ricinoleic}\\\text{acid.}}}{C^{18}H^{34}O^3} + 2KHO = \underset{\substack{\text{Heptylic}\\\text{alcohol.}}}{C^7H^{16}O} + \underset{\substack{\text{Sebate of}\\\text{potassium.}}}{C^{10}H^{16}K^2O^4} + \underset{\substack{\text{Marsh}\\\text{gas.}}}{CH^4}$$

The evolution of marsh gas, which the latter equation supposes, has not, however, been observed: the gas evolved appears to be in all cases pure hydrogen. **Städeler's** analysis of the alcohol agrees very closely with the formula of heptylic alcohol. Similar results have been obtained by **Petersen** (Ann. Ch. Pharm. cxvii. 69), who analysed the alcohol after carefully freeing it from methyl-œnanthyl, and also some of its derivatives, all of which gave results agreeing with the 7-carbon formulæ. On the other hand, **Dachauer** (Ann. Ch. Pharm. cvi. 269), from his analyses of the carefully-purified alcohol and several of its derivatives, has come to the conclusion that the volatile products of the reaction are methyl-œnanthyl and octylic alcohol, the formation of the latter differing from that of the former, only by the evolution of 2 at. hydrogen instead of four:

$$\underset{\substack{\text{Ricinoleic}\\\text{acid.}}}{C^{18}H^{34}O^3} + 2KHO = \underset{\text{Octylic alcohol.}}{C^8H^{18}O} + \underset{\substack{\text{Sebate of}\\\text{potassium.}}}{C^{10}H^{16}K^2O^4} + H^2$$

From these various statements it appears probable that both heptylic and octylic alcohol may be produced in this reaction. It must be observed, however, that the percentage of carbon in the two alcohols differs by only 1·4 per cent., and that the percentage of carbon in heptylic alcohol (72·4) might easily be raised to that of octylic alcohol (73·8) by the admixture of a certain quantity of methyl-œnanthyl, which contains more carbon than either of them (75·0 per cent.), and is very difficult to separate from the alcohol. It is possible, therefore, that the alcohol obtained may be in all cases the heptylic, but that some chemists who have analysed it have not succeeded in completely removing the methyl-œnanthyl. On the other hand, assuming the received formula of ricinoleic acid to be correct (and it is confirmed by Petersen's analyses, *loc. cit.*), the formation of the 7-carbon alcohol, together with sebacic acid, does not account for the whole of the carbon, unless we suppose marsh gas to be evolved, which has not been observed by any one. The subject, therefore, requires further investigation.

Preparation of Heptylic alcohol from Castor-oil.—The oil is saponified with caustic soda, and the ricinoleate of sodium, separated in the usual way by common salt, is distilled by small portions with excess of caustic soda, as long as the distillate continues to pass over colourless. The portion collected between 170° and 180° is rectified over solid potash, washed, and shaken up with a concentrated solution of acid sulphite of sodium; and the thick pulp which forms after a while is separated from the mother-liquor by pressing it and transferring it to a moist filter. The whole mass is then repeatedly agitated with ether, in which the alcohol is soluble, but the compound of the acetone with the alkaline sulphite is insoluble. The ethereal solution is then filtered off; the ether removed by distillation, the residual oil again mixed with strong solution of acid sulphite of sodium, and set aside for several days; the watery liquid again separated from the mass, which has now become gelatinous; this mass is exhausted with ether; and the oil obtained from this ethereal solution is again treated several times with sulphite of sodium, being ultimately left in contact with it for several weeks, or as long as any small quantity of gelatinous precipitate continues to separate. The oil finally obtained after evaporating the ether is rectified over a small quantity of hydrate of potassium, then washed with water and dried. The product thus obtained is heptylic alcohol. (Petersen.)

Properties.—Heptylic alcohol is a colourless oily liquid, insoluble in water, soluble in common alcohol and in ether. Specific gravity 0·819 at 23° (Städeler). Vapour-density 4·34 (Petersen), 4·16 (Faget), 4·019, by determination in an atmosphere of hydrogen (Railton): by calculation (2 vol.) = 4·04. Boiling point 179° (Wills), between 177 and 177·5° (Städeler), 178·5° (Petersen), 165° (Bouis and Carlet), between 155° and 160° (Faget). These differences, as with the chloride, indicate the existence of two modifications of the alcohol. The calculated boiling point, according to Kopp's law, is 173° (p. 90), so that the heptylic alcohol obtained from castor-oil appears to be the normal compound, whereas the alcohol obtained from brandy fusel-oil, and that produced from œnanthol, appear to correspond with Wanklyn and Erlenmeyer's β-hexylic alcohol, inasmuch as the latter boils at 134°, and $137 + 19 = 156$.

The following table exhibits the composition of heptylic alcohol as determined by calculation and by analysis:

	Calculation.		Wills.	Städeler, *mean.*	Petersen.	Faget.	Schorlemmer, *mean.*
C^7	84	72·4	72·79	72·33	72·21	72·43	72·25
H^{16}	16	13·8	13·67	13·55	13·99	13·84	14·24
O	16	13·8	13·54	14·12	13·80	13·73	13·51
$C^7H^{16}O$	116	100·0	100·00	100·00	100·00	100·00	100·00

Faget's alcohol was obtained from brandy fusel-oil (p. 144); Schorlemmer's was prepared from hydride of heptyl obtained from Boghead naphtha; the other three from castor-oil. Petersen observes that the purification of the alcohol did not always succeed so completely as in the sample whose analysis is above given; in one specimen he found 72·95 per cent. carbon and 13·37 hydrogen. Bouis, Moschnin, and Dachauer, as already observed, have obtained, by their analyses of the castor-oil alcohol, results agreeing more nearly with the formula $C^8H^{18}O$, viz. Bouis, 73·5 C, 13·9 H; Moschnin, 73·6 C, 13·8 H; Dachauer, 73·8 C, 13·9 H (calc. 73·8 C, 13·8 H). See OCTYLIC ALCOHOL.

Decompositions.—1. Heptylic alcohol distilled with *chloride of zinc*, yields heptylene, C^7H^{14} (Bouis and Carlet).—2. Heated with *potash-lime*, it gives off hydrogen, and is converted into œnanthylic acid, $C^7H^{14}O^2$ (Faget).—3. With *pentachloride of phosphorus*, it yields chloride of heptyl (Petersen), and with *iodine* and *phosphorus*, iodide of heptyl (Schorlemmer).—4. With *sulphuric acid*, it forms heptyl-sulphuric acid, $C^7H^{16}SO^4$ (Petersen).

HEPTYL, HYDRIDE OF. $C^7H^{16} = C^7H^{15}.H$.—This compound occurs, together with several of its homologues, in rectified American petroleum (Pelouze and Cahours, Compt. rend. lvi. 505; Ann. Ch. Pharm. cxxvii. 196.—Schorlemmer, Proc. Lit. Phil. Soc. Manchester, March 13, 1863; Chem. Soc. J. xvi. 216) and in the light oil obtained from the tar of cannel-coal (Schorlemmer, Chem. Soc. J. xv. 423): it is also produced, together with some of its homologues and other hydrocarbons, by distilling amylic alcohol with chloride of zinc. (A. Wurtz, Compt. rend. lvi. 1164, 1246; Ann. Ch. Pharm. cxxviii. 225.)

1. Rectified American petroleum may be separated by fractional distillation into the hydrides of twelve alcohol-radicles, from hydride of tetryl, C^4H^{10}, boiling at a few degrees above 0°, to hydride of pentadecatyl, $C^{15}H^{32}$, boiling between 255° and 260°, besides others of still higher boiling point (see HYDRIDES). When the liquid which remains after the separation of the hydrides of amyl, boiling at 30°, and hexyl, at 68°, is submitted to further rectification, the temperature remains constant for some time between 90° and 96°; and if the portion which passes over between these temperatures be collected apart and again carefully rectified, the quantity of material being somewhat considerable, a product may be isolated which, after purification by shaking it up with very concentrated sulphuric acid, washing with dilute carbonate of sodium, and dehydration with chloride of calcium, boils between 92° and 94°: this is hydride of heptyl. (Pelouze and Cahours.)

2. The mixture of oils obtained by distilling cannel-coal at as low a temperature as possible, is left in contact for several days with an equal volume of sulphuric acid, and frequently shaken; the oil is then poured off, washed with water, and distilled; and the distillate, consisting of benzene and benzylene (toluene), together with the hydrides of the alcohol-radicles, is repeatedly shaken with strong nitric acid, to convert the benzene and benzylene into nitro-compounds, until, on adding water to the liquid, no further separation of these compounds occurs. The portion unacted upon by the nitric acid is then washed with water, dried over potash, and repeatedly rectified over sodium. The liquid thus obtained yields by fractional distillation, hydride of amyl, C^5H^{12}, boiling at

39°—40° C., hydride of hexyl at 68°—70° hydride of heptyl at 98°—99°, and hydride of octyl at 119°—120°. (Schorlemmer.)

3. The distillate obtained by heating amylic alcohol with chloride of zinc consists of amylene and compounds polymeric with it, together with hydride of amyl, and smaller quantities of the hydrides of hexyl, heptyl, &c., up to $C^{10}H^{22}$. Heptylene and hydride of heptyl are contained in the portion of the distillate boiling between 85° and 95°, and may be separated by converting the heptylene into a bromide and distilling, the hydride of heptyl then passing over first. (Wurtz.)

Hydride of heptyl is a thin mobile liquid, having a faint but pleasant odour, and burning with a slightly smoky flame. Specific gravity 0·7122 at 16°; 0·709 at 17·5° (Schorlemmer). Boils at 98°—99° (Schorlemmer), at 92°—94° (Pelouze and Cahours). Vapour-density by experiment, 3·49—3·59 (Schorlemmer), 3·616 (Pelouze and Cahours); by calculation (2 vol.) = 3·46. It gives by analysis 83·93 and 84·0 per cent. carbon, 16·13 and 16·1 hydrogen, the formula requiring 84 C and 16 H (Schorlemmer). By *chlorine*, and more quickly by *chloride of iodine*, it is converted into chloride of heptyl. Chlorine passed into hydride of heptyl forms, besides chloride of heptyl, small quantities of some other chlorine-compounds, which, when distilled with sodium, yield a liquid boiling at 95°—100°, and having the odour and composition of heptylene (Schorlemmer, Chem. Soc. J. xv. 424). With *bromine*, hydride of heptyl appears to yield bromide of heptyl (p. 144).

HEPTYL, IODIDE OF. $C^7H^{15}I$.—Obtained by the action of iodine and phosphorus on heptylic alcohol (Schorlemmer, Chem. Soc. J. xvi. 219.—Petersen, Ann. Ch Pharm. cxviii. 74). It is a colourless liquid, heavier than water, quickly turning brown in contact with the air, boiling at 190° (Schorlemmer), 192° (Petersen). Composition by analysis, 37·19 per cent. C, 6·73 H, and 56·18 I; by calculation, 37·17 C, 6·64 H, and 56·19 I. It is instantly decomposed by alcoholic nitrate of silver, the whole of the iodine being separated as iodide of silver. (Schorlemmer.)

HEPTYL, SULPHYDRATE OF. $C^7H^{16}S = C^7H^{15}.H.S$.—Obtained by heating chloride of heptyl with alcoholic sulphydrate of potassium in a sealed tube. Colourless liquid, boiling between 155° and 158°, having a mercaptan-like, as well as aromatic, odour, and exhibiting all the characteristic reactions of the mercaptans. (Schorlemmer.)

HEPTYLAMINE. $C^7H^{17}N = N.H^2.C^7H^{15}$.—Obtained: 1. By saturating iodide of heptyl with ammonia, heating the solution in the oil-bath, and removing the iodine with oxide of silver (Petersen, *loc. cit.*).—2. By heating chloride of heptyl with ammonia in sealed tubes to 120° for several days. The chlorides of the different heptyl-ammoniums are then formed, but chiefly chloride of heptyl-ammonium, $C^7H^{18}Cl$. This salt dissolves easily in water and alcohol, and crystallises in small scales. When distilled with caustic potash, it yields heptylamine, as a light oily liquid, having an ammoniacal aromatic odour, a burning taste, and boiling at 145°—147°. It is moderately soluble in water, and separates out again on addition of caustic potash. (Schorlemmer, Chem. Soc. J. xvi. 221.)

The *platinum-salt*, $C^7H^{18}NCl.PtCl^2$, is slightly soluble in cold water, freely soluble in hot water, also in alcohol and ether, crystallising from these solutions in small yellow scales. Gives by analysis 30·7 per cent. platinum (Schorlemmer); 30·9 (Petersen); calc. 30·79.

HEPTYLAMYLIC ETHER. $C^{12}H^{26}O = C^7H^{15}.C^5H^{11}.O$. *Amylœnanthylic ether.*—Produced by the action of heptylate of sodium on an equivalent quantity of iodide of amyl, and obtained, though with some difficulty, by submitting the product to fractional distillation, as a colourless mobile liquid, boiling between 220° and 221°. Specific gravity = 0·608 at 20°. Vapour-density: obs. = 6·57; calc. (2 vols.) = 6·45. Analysis 77·0 per cent. C, and 13·8 H. Calculated composition, 77·4 C, 14·0 H, and 8·6 O. (Wills, Chem. Soc. J. vi. 316.)

HEPTYLENE. C^7H^{14}. *Oenanthylene.*—This hydrocarbon, homologous and polymeric with ethylene, is contained, together with others of the series C^nH^{2n}, and hydrocarbons belonging to the series C^nH^{2n+2} and C^nH^{2n-6}, in the light oil obtained by the distillation of Boghead coal. By treating this oil with bromine in presence of water, the hydrocarbons C^nH^{2n} are converted into heavy oily bromides, while the other hydrocarbons remain unaltered and may be distilled off. The remaining liquid separates, on standing, into three layers, the upper consisting of water with a little hydrobromic acid, the middle of the organic bromides, and the lowest of aqueous hydrobromic acid. The middle layer separated and distilled with alcoholic potash and with sodium, yields the hydrocarbons C^nH^{2n}. The brominated oils obtained from the fractions of the original coal-oil which boiled between 71° and 77° and between 82° and 88°, yielded respectively hexylene boiling at 71° and heptylene boiling at 99° (Greville Williams, Phil. Trans. 1857 [3] 737; Ann. Ch. Pharm. cviii. 384). Heptylene is likewise obtained:—1. By decomposing chloride of heptylene with sodium at a gentle heat

The sodium is added by small quantities; the liquid distilled off as soon as the quantity of chloride of sodium becomes so great as to interfere with the action; and the distillate is treated with fresh sodium, the last traces of chlorine being removed by repeatedly rectifying the product over perfectly bright sodium (Limpricht, Ann. Ch. Pharm. ciii. 80). The heptylene which Schorlemmer obtained by treating with sodium the chlorinated compounds produced, in addition to chloride of heptyl, by the action of chlorine on hydride of heptyl (p. 144), probably also resulted from the decomposition of chloride of heptylene.—2. By distilling heptylic alcohol with chloride of zinc: $C^7H^{16}O - H^2O = C^7H^{14}$ (Bouis and Carlet).—3. By heating chloride of heptyl with strong aqueous potash to 180° in sealed tubes for several days (Schorlemmer, p. 144).—Bouis, in 1855, by distilling œnanthol with strong sulphuric acid, obtained a hydrocarbon agreeing in composition with the empirical formula of the olefines, CH^2, and supposed by him to be heptylene; but, as it boiled at 50°, it was probably either a lower member of the series, or a mixture.

Heptylene is a colourless mobile liquid, having a peculiar alliaceous odour; soluble in alcohol. Boils at 95° (Schorlemmer), at 99° (Gr. Williams). Specific gravity 0·718 at 18° (Williams). Vapour-density, obs. = 3·320 (Williams); calc. (2 vol.) = 3·386.

	Calculation.		Limpricht.	Schorlemmer.	
C^7	84	85·71	85·9	85·6	85·66
H^{14}	14	14·29	14·1	14·6	14·00
C^7H^{14}	98	100·00	100·0	100·2	99·66

Bromide of Heptylene. $C^7H^{14}Br^2$.—Obtained by direct combination. It is a liquid, heavier than water, which decomposes on distillation, with blackening and evolution of hydrobromic acid, but volatilises in presence of aqueous vapour, condensing as a nearly colourless liquid having the odour of bromide of ethylene. Gives by analysis 62·26 and 62·23 bromine, the formula requiring 62·01. (Schorlemmer.)

Chloride of Heptylene. $C^7H^{14}Cl^2$.—Produced by the action of pentachloride of phosphorus on œnanthol. When 1 at. œnanthol is gradually allowed to flow into 1 at. pentachloride of phosphorus contained in a tubulated retort, great heat is evolved, and a portion of the resulting oxychloride of phosphorus distils over immediately. As soon as the decomposition of the pentachloride is complete, the liquid is subjected to fractional distillation, the portion which boils above 150° being collected apart as long as it passes over colourless; in the retort there remains a small quantity of a brown thick liquid. The last distillate is washed with water to remove adhering oxychloride of phosphorus; and the oil which floats on the water is shaken up with acid sulphite of sodium, to remove undecomposed œnanthol, then dried with chloride of calcium, and rectified, the portion which boils between 180° and 200° being collected apart: on again rectifying this portion, pure chloride of heptylene passes over at 187°.

Chloride of heptylene is a transparent, colourless, mobile liquid, lighter than water, having a not unpleasant odour, like that of œnanthol. It boils at 191° (corrected). Gives by analysis 48·85 per cent. C, 8·00 H, and 42·05 Cl; the formula requiring 49·4 C, 8·2 H and 42·4 Cl.

When gently heated with *sodium*, it is decomposed with violence, yielding heptylene and chloride of sodium.—Boiled for some time with ethylate of sodium or alcoholic solution of potash, it is resolved into hydrochloric acid, chlorheptylene, $C^7H^{13}Cl$, and a hydrocarbon, probably C^7H^{12}:

$$C^7H^{14}Cl^2 - HCl = C^7H^{13}Cl\text{; and } C^7H^{14}Cl^2 - 2HCl = C^7H^{12}$$

It is not perceptibly decomposed by acetate of silver, even when continuously boiled with it, or heated to 250° in sealed tubes. (Limpricht, Ann. Ch. Pharm. ciii. 80.)

Chlorheptylene. $C^7H^{13}Cl$.—Obtained by the action of alcoholic potash or ethylate of sodium on chloride of heptylene. A very concentrated alcoholic solution of potash is distilled upwards with chloride of heptylene for a considerable time (the decomposition of 15 grammes of the chloride takes about a week);—or chloride of heptylene and ethylate of sodium are heated together in a sealed tube to 250°. The liquid obtained by either process is diluted with water, which separates impure chlorheptylene; and this crude product is dried by means of chloride of calcium and then subjected to fractional distillation. It begins to boil at 100°, the boiling point slowly rising to 150°, where it remains constant for a while and ultimately rises to 190°. The liquid which passes over below 100° is a hydrocarbon (*see below*); that which distils at 152° is chlorheptylene, and above that temperature the product consists chiefly of undecomposed chloride of heptylene. The complete separation of these liquids can only be effected by repeated rectification.

Chlorheptylene is a liquid resembling chloride of heptylene, having a similar odour, and boiling at 155° (corrected). It gives by analysis 63·5 per cent. C, 9·7 H, and 26·8 Cl, the formula requiring 63·2 C, 9·7 H and 27·1 Cl.

Sodium remains unaltered in chlorheptylene at ordinary temperatures; but on heating the liquid, a violent action suddenly takes place, chloride of sodium being formed, together with a hydrocarbon, probably C^7H^{12}.—The same hydrocarbon appears to be produced by the action of alcoholic potash on chloride of heptylene (see above). (Limpricht, Ann. Ch. Pharm. cii. 82.)

Hydriodate of Heptylene. $C^7H^{15}I = C^7H^{14}.HI$.—Obtained by heating heptylene with hydriodic acid in sealed tubes to 100° for twelve hours. It closely resembles iodide of heptyl, but boils at about 170°, or 20° lower than the latter. It soon turns brown when exposed to the air. Precipitated by alcoholic nitrate of silver, it yielded a quantity of iodide of silver corresponding to 55·73 per cent. iodine (calc. 56·19); and the filtrate, on being mixed with water, yielded a small quantity of a fragrant liquid, which consisted wholly or in a great part of nitrate of heptylene, $C^7H^{14}.NO^3H$, as on adding an alcoholic solution of potash, and heating gently, an abundant precipitate of nitrate of potassium was formed. (Schorlemmer, Chem. Soc. J. xvi. 220.)

HEPTYL-ETHYLIC ETHER. $C^9H^{20}O = C^7H^{15}.C^2H^5.O$. *Ethyl-œnanthylic ether.* (Wills, Chem. Soc. Qu. J. vi. 312;* Petersen, Ann. Ch. Pharm. cxviii. 75).—Prepared by the mutual action of iodide of ethyl and heptylate of sodium in equivalent proportions:

$$C^7H^{15}NaO + C^2H^5I = NaI + C^7H^{15}.C^2H^5.O.$$

It is a colourless mobile liquid, having a faint odour, and burning with a bright flame; insoluble in water, easily soluble in alcohol and ether. Boils at 177° (Wills). Specific gravity = 0·791 at 16°. Vapour-density, obs. = 5·095 (Wills); calc. (2 vol.) = 4·99.

	Calculation.		Wills.	Petersen.
C^9	108	75·00	75·16	74·44
H^{20}	20	13·88	14·44	14·40
O	16	11·12	10·40	11·16
$C^9H^{20}O$	144	100·00	100·00	100·00

HEPTYLIC ALDEHYDE. Syn. with Œnanthol. (*q. v.*)

HEPTYL-METHYLIC ETHER. $C^8H^{18}O = C^7H^{15}.CH^3.O$. *Methyl-œnanthylic ether.* (Wills, Chem. Soc. J. vi. 314.)—Obtained by the action of iodide of methyl on heptylate of sodium. It is a thin mobile liquid, having a strong odour, insoluble in water, easily soluble in alcohol and in ether. Boiling point between 160·5° and 161°. Specific gravity = 0·830 at 16·5°. Vapour-density (obs.) about 4·2; calc. (2 vol.) = 4·5. A specimen not quite pure gave by analysis 73·15 per cent. C, and 14·09 H, the formula requiring 73·85 C and 13·85 H.

HEPTYL-SULPHURIC ACID. $C^7H^{16}SO^4 = \left.\begin{matrix}(SO^2)''\\ C^7H^{15}\\ H\end{matrix}\right\}O^2$. (Petersen, Ann. Ch. Pharm. cxviii. 72.—Bouis and Carlet, *ibid.* cxxiv. 254.)—When 2 pts. of heptylic alcohol are cautiously mixed with 1 pt. sulphuric acid, the mixture being kept cool so as to prevent the formation of sulphurous acid, the liquid ultimately separates into two layers, the upper of which contains heptyl-sulphuric acid. On neutralising it with carbonate, and at last very carefully with hydrate of barium, and concentrating at a gentle heat, heptyl-sulphate of barium separates in small, white, flexible, and generally scaly crystals, having a pearly lustre and bitter taste, very soluble in water, and not precipitated from the aqueous solution by alcohol or ether. The solution decomposes by evaporation unless the temperature be kept very moderate. The dry salt is permanent in the air, but, according to Petersen, begins to decompose at 80°, turning first red, then black, and emitting a very strong odour. According to Bouis and Carlet, on the other hand, it may be heated to 100° without decomposition. According to the mean results of Petersen's analyses, the salt dried over oil of vitriol contains 30·97 per cent. C, 6·19 H, 25·10 Ba, and 11·73 S, agreeing nearly with the formula $2C^7H^{15}BaSO^4.H^2O$, which requires 30·83 C, 5·87 H, 25·14 Ba, 11·74 S, and 26·42 O.

HERAPATHITE. Syn. with Sulphate of Iodoquinine. (See Quinine.)

HERCYNITE. An iron spinel, $Fe^2O.Al^4O^3 = \left.\begin{matrix}Fe\\ (Al^2)'''\end{matrix}\right\}O^2$. Specific gravity 3·91—3·95. (See Spinel.)

HERDERITE. A very rare mineral, consisting of anhydrous phosphate of aluminium, and phosphate with fluoride of calcium; not yet analysed quantitatively. The crystals are trimetric. Hardness = 5. Specific gravity = 2·985. It resembles apatite in colour and lustre, but is distinguished by its lower specific gravity. Soluble in hydrochloric acid. Melts before the blowpipe to a white bead, with slight intumescence. (Dana, ii. 410.)

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* The compound obtained by Wills is described at p. 542, vol. ii. as octyl-ethylic ether; but the balance of evidence is certainly in favour of the supposition that it contains heptyl, not octyl.

HERMANNITE. See RHODONITE.

HERRERITE. A mineral from Albarradon in Mexico, said by Herrera (J. pr. Chem. viii. 514) to contain 35·58 per cent. tellurium, 12·32 oxide of nickel, and 31·86 carbonic acid. According to Genth, however (*ibid.* lxvi. 475), it is a cupriferous zinc-spar, containing 93·74 per cent. Zn^2CO^3, 3·42 Cu^2CO^3, 1·50 Mn^2CO^3, 1·48 Ca^2CO^3, and 0·29 Mg^2CO^3.

HERSCHELITE. A mineral from Aci reale and Aci Castello in Sicily, having the same general formula as lime-harmotome (p. 14), viz. $M^2O.Al^4O^3.4SiO^2 + 5H^2O$, or $(M\mathit{al}^3)Si^2O^8 . \frac{5}{2}H^2O$, agreeing also in general formula with gmelinite (ii. 924) excepting in the amount of water, and crystallising, like the latter, in the hexagonal system.

Analyses 1 and 2 are of the mineral from Aci reale, by Damour (Ann. Ch. Phys. [3] xiv. 97); 3, 4, from Aci Castello, by v. Waltershausen, (*Vulkanische Gesteine*, p. 260):

	SiO^2	Al^4O^3	Fe^4O^3	Ca^2O	Mg^2O	Na^2O	K^2O	H^2O.
1.	47·39	20·90	. .	0·38	. .	8·33	4·39	17·84 = 99·23
2.	47·46	20·18	. .	0·25	. .	9·35	4·17	17·65 = 99·06
3.	45·89	18·20	1·14	4·84	0·35	5·72	3·72	17·86 = 97·72
4.	47·03	20·21	1·14	4·66	0·49	4·82	2·03	17·86 = 98·24

These analyses lead to the formulæ:

Damour.

$$\left.\begin{matrix}\frac{3}{4}Na^2O\\ \frac{1}{4}K^2O\end{matrix}\right\} SiO^2.(Al^4O^3.3SiO^2) + 5 \text{ aq.}$$

v. Waltershausen.

$$\left.\begin{matrix}\frac{4}{9}Ca^2O\\ \frac{4}{9}Na^2O\\ \frac{1}{9}K^2O\end{matrix}\right\} SiO^2.(Al^4O^3.3SiO^2) + 5 \text{ aq.}$$

According to v. Waltershausen, herschelite does not occur at Aci reale.

HESPERIDIN. A substance discovered by Lebreton (J. Pharm. xiv. 377), and contained in many fruits of the genus *Citrus.* It is most readily prepared from unripe Seville oranges, by removing the green rind and the inner part of the fruit, treating the white spongy inner coating with water at a temperature of 25 to 30°; concentrating the liquid, neutralising it with lime-water, and evaporating to a syrup; treating the residue with alcohol of 40 per cent.; then filtering, distilling off the alcohol, and agitating the bitter granular residue with 20 times its weight of distilled vinegar. The liquid on standing deposits hesperidin in warty masses, which may be washed with water and recrystallised from boiling alcohol.

Hesperidin thus purified forms white, silky laminæ, inodorous, and having a bitter taste; sparingly soluble in cold *alcohol*, very soluble in boiling alcohol, insoluble in *ether*; dissolves in 60 pts. of boiling *water*, and separates again on cooling. The solutions are neutral to vegetable colours. It is soluble in warm concentrated *acetic acid*, insoluble in *oils*.

Hesperidin is decomposed by prolonged boiling with *water*, and then floats on the surface like melted wax. It is readily dissolved by caustic *alkalis*. Strong *sulphuric acid* dissolves it with orange-colour, gradually changing to red. Hot *nitric acid* converts it into oxalic acid and a bitter substance. The alcoholic solution is not precipitated by *acetate of lead*, but forms a brown precipitate with *ferric sulphate*.

Wiedemann has described, under the name *hesperidin*, a substance obtained from unripe oranges, differing from that above described in some respects, especially in not being soluble in alcohol.

HESSITE. Telluric silver. (See TELLURIUM.)

HESSONITE. Syn. with ESSONITE (ii. 507).

HETEPOZITE. See HETEROSITE.

HETEROCLINE or *Marceline.* A silicate of manganese occurring at St. Marcel in Piedmont, in oblique rhombic prisms of 128° 16′, and containing 10·76 per cent. SiO^2, 85·87 Mn^4O^3, 3·38 Fe^4O^3, 0·61 Ca^2O, and 0·44 K^2O = 100·30. (Evreinoff, Pogg. Ann. xlix. 204.)

HETEROMERITE. An altered form of idocrase from Slatoust in Siberia, containing, according to v. Hauer, 43·29 SiO^2; 23·17 Al^4O^3; 6·10 Fe^4O^3; 23·78 Ca^2O, and 3·05 Mg^2O. Colour light green.

HETEROMORPHISM. The property, sometimes observed in compounds, of crystallising in different forms, though containing equal numbers of atoms similarly grouped. Such is the case with *sulphate of zinc*, $\left.\begin{matrix}SO^2\\ Zn^2\end{matrix}\right\} O^2 + \frac{7}{2}H^2O$, and *ferrous sulphate*, $\left.\begin{matrix}SO^2\\ Fe^2\end{matrix}\right\} O^2 + \frac{7}{2}H^2O$; the former crystallising in the monoclinic, the latter in the trimetric system. The cause of this difference in the examples just cited is probably that the elements—iron and zinc—are not isomorphous.

HETEROMORPHITE. *Feather ore.*—A sulphantimonite of lead, $Sb^2S^3.2Pb^2S$, which occurs in capillary forms resembling a cobweb; also massive. Specific gravity 5·67 to 5·9. Hardness 1 to 3. Lustre dull metallic. Colour lead-grey to steel-grey, sometimes iridescent. It is found at Wolfberg in the Eastern Hartz; also at Andreasberg and Clausthal; at Freiberg and Schemnitz; in the Anhalt at Pfaffenberg and Meiseberg; and in Tuscany, near Bottino. (Dana, ii. 76.)

HETEROSITE or *Heteposite.* A hydrated phosphate of iron and manganese, found near Limoges, in dark brown or black masses, containing, according to Dufrénoy's analyses, 4 1·77 p. c. P^2O^5, 34·89 Fe^2O, 17·57 Mn^2O, 4·40 H^2O, and 0·22 SiO^2 (= 98·85), whence Rammelsberg (*Mineralchemie*, p. 331) deduces the formula $3(5M^2O.2P^2O^5) + 3\left[\left.\begin{matrix}\frac{2}{3}Fe^2O\\ \frac{1}{3}Mn^2O\end{matrix}\right\}^{5} 2P^2O^5\right] + 10$ aq.

The same name is applied to an altered triphyllin from Chanteloub, Limoges, of brownish violet colour, specific gravity 3·41, and containing 32·18 p. c. P^2O^5, 31·46 Fe^4O^3, 30·01 Mn^4O^3, and 6·35 water (= 100), whence the formula $5M^4O^3.3P^2O^5 + 5$ aq. (Rammelsberg, *loc. cit.*)

HEULANDITE. See STILBITE.

HEVEENE. The least volatile part of the products of the dry distillation of caoutchouc and gutta percha. It is an oily hydrocarbon, of an amber-yellow colour, acrid taste, and specific gravity 0·921 at 21°. Boils at 315°. Mixes in all proportions with alcohol, ether, and oils, both fat and volatile. It rapidly absorbs chlorine, and acquires thereby the consistence of wax. It is partly resinised by sulphuric acid, and then converted into an oil which boils at 228°, and is not attacked by strong acids (Bouchardat, Ann. Ch. Pharm. xxvii. 30). According to Greville Williams, it is probably polymeric with isoprene and caoutchin (ii. 961).

HEXACHLORXYLIN. A product of the action of chlorine on hydrate of phenyl. (See PHENYL.)

HEXACROLEIC ACID. $C^{18}H^{24}O^6$.—An acid polymeric with acrolein, and produced by dropping that liquid into an alcoholic solution of potash. The solution becomes heated to the boiling point; and on addition of an acid, yields hexacroleic acid as a yellow, amorphous, feebly acid substance, soluble in alkalis, alcohol and ether; insoluble in water, easily fusible, but not volatile without decomposition. Most of its salts are insoluble in water. (Claus, Ann. Ch. Pharm. suppl. ii. 117.)

HEXAMETAPHOSPHORIC ACID. See PHOSPHORIC ACID.

HEXAMETHYLENAMINE. $C^6H^{12}N^4 = N\left\{\begin{matrix}N(CH^2)^2\\ N(CH^2)^2\\ N(CH^2)^2\end{matrix}\right.$.—A volatile crystalline base produced by the action of ammonia on dioxymethylene (Buttlerow, Ann. Ch. Pharm. cxv. 322). See METHYLENAMINES.

HEXETHYLENIC ALCOHOL. See ETHYLENE, HYDRATES OF (ii. 576).

HEXMETHYL-ETHYLENE-DIPHOSPHONIUM. See PHOSPHORUS-BASES.

HEXYL. *Caproyl.* $C^{12}H^{26} = \begin{matrix}C^6H^{13}\\ C^6H^{13}\end{matrix}$.—The sixth alcohol-radicle of the series C^nH^{2n+1}. It is produced by the electrolysis of œnanthylic acid:

$$C^7H^{14}O^2 = C^6H^{13} + H + CO^2.$$

To prepare it, a solution of œnanthylate of potassium is decomposed by a voltaic current, and the oil which separates is dried over chloride of calcium, and then distilled with alcoholic potash, which retains œnanthylic acid, while the hexyl passes over with the vapours of alcohol, and may be purified by washing with water and rectification (Brazier and Gossleth, Chem. Soc. J. iii. 210). Wurtz (Ann. Ch. Phys. [3] xliv. 275), by electrolysing a mixture of 100 pts. œnanthylic and 120 pts. valeric acid, neutralising with potash and cooling to 0°, obtained an oil which, after desiccation by chloride of calcium, yielded by fractional distillation, tetryl (C^4H^9), boiling between 100° and 140°, tetryl-hexyl ($C^4H^9.C^6H^{13}$), between 140° and 180°, and a portion boiling between 180° and 220°, consisting chiefly of hexyl.

Hexyl is a colourless oily liquid, of specific gravity 0·7574 at 0°. It boils at 202°, yielding a vapour whose density is 5·983 (Wurtz); calc. (2 vol.) = 5·8979. It is insoluble in water, but soluble in alcohol and ether.

It is not attacked by sulphuric acid, and may be distilled without alteration with moderately concentrated nitric acid; but by repeated distillation with a mixture of sulphuric and nitric acids, it is converted into an acid, probably caproic acid. It is scarcely attacked by bromine, even in sunshine. Chlorine attacks it strongly, even in diffused daylight; hydrochloric acid being evolved, and a viscid substance formed, which gives off hydrochloric acid when distilled, and leaves a residue of charcoal. (Brazier and Gossleth.)

The compounds of hexyl were hardly known before the year 1861, the alcohol having been barely identified by Faget, in fusel-oil, in 1854 (Compt. rend. xxxvii. 730). At present, the known sources of hexyl-compounds are: (1) fusel-oil, containing the alcohol; (2) mannite and melampyrin, which, when reduced with hydriodic acid, give iodide of hexyl; and (3) petroleum and coal-tar oil, which contain hydride of hexyl. Whether the hexyl-compounds obtained from (1) and (3) are identical, is still an open question; but, without doubt, those derived from (2) are essentially different from the hexyl-compounds either of fusel-oil or of petroleum. The hexyl-compounds of fusel-oil and of petroleum have been distinguished by the prefix *Alpha*, those of mannite or melampyrin by *Beta*. The former compounds, so far as they have been yet examined, present the very closest analogies to those of the ethyl series; the latter depart in many ways from this standard: thus, they show a great tendency to evolve their olefine during reactions; and their alcohol has too low a boiling point, and when oxidised with dilute chromic acid, does not yield caproic acid, but breaks up into carbonic acid, water, butyric and acetic acids.

The hexyl-compounds derive peculiar interest from their having the same carbon-condensation as the sugars, and from their standing in close relation thereto, as the reaction of hydriodic acid with mannite proves, mannite being, as has long been known, a product of the reduction of glucose (ii. 864).

Berthelot has already remarked upon the peculiar readiness to react shown by tritylene. It is not unworthy of remark, that hexylene, which is paratritylene, likewise displays extraordinary energy.

Acetates of Hexyl.—α *Hexyl-acetate* is prepared by the action of α iodide of hexyl upon acetate of silver. It is a colourless liquid, lighter than water, and boiling at about 145° C. By the action of caustic potash, it has been transformed into an alcohol, boiling at about 150°. (Cahours and Pelouze, Compt. rend. liv. 1245.)

β *Hexyl-acetate* is prepared by distilling β hexyl-sulphuric acid with a great excess of glacial acetic acid:—

$$\left.\begin{matrix}\beta\,C^6H^{13}\\ H\end{matrix}\right\}SO^4 \;+\; \left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}O \;=\; \left.\begin{matrix}H\\ H\end{matrix}\right\}SO^4 \;+\; \left.\begin{matrix}C^2H^3O\\ \beta\,C^6H^{13}\end{matrix}\right\}O.$$

It is an oil lighter than water, and very insoluble in water, having a peculiar smell, unlike the usual smell of an acetate of an alcohol-radicle. Boiling point 156°. It distils without decomposition. Digestion at 100°, with an alcoholic solution of potash, transforms it into β hexylic alcohol. Unlike β $C^6H^{13}I$, it yields no hexylene on digestion with alcoholic solution of potash. Sp. gr. at 0° = ·8778 : at 50° = ·8310; therefore expansion-coefficient for 50° = ·0563. It forms a double compound with $Na\beta C^6H^{13}O$ (beta-hexylate of sodium—the body produced by treating β hexylic alcohol with sodium), which double compound is decomposed by water, giving β hexylic alcohol.

Hexyl-alcohols.—α *Hexyl-alcohol* (caproic alcohol), α $C^6H^{14}O$, was found by Faget, in fusel-oil (1854), but not purified by him. Cahours and Pelouze obtained it from hydride of hexyl, by converting that compound into α iodide of hexyl, thence forming α acetate of hexyl; thence, by means of caustic potash, the alcohol. The α hexyl-alcohol thus prepared boils at about 150°, and smells like amylic alcohol. (Compt. rend. liv. 1245.)

α hexylic alcohol yields caproic acid by oxidation. (Faget.)

β *Hexyl-alcohol*, β $C^6H^{14}O$.—Prepared by digesting β iodide of hexyl with oxide of silver and water: the β alcohol is then formed, together with β hexylic ether, and β hexylene. Or better, by shaking up β hexylene with sulphuric acid (previously diluted with one-third its volume of water), by which means β hexyl-sulphuric acid is produced, and this, distilled with a large excess of water, yields β hexyl-alcohol. It is a viscid liquid, having a refreshing, pleasant smell, very unlike that of amylic alcohol; boils at 137°, under bar. pressure of 755·5 millimetres. Specific gravity at 0° = 0·8327; at 16° = 0·8209; at 99° = 0·7482. It therefore expands somewhat rapidly.

Concentrated *sulphuric acid* converts it into para-hexylene, even at 0°, and does not form any hexyl-sulphuric acid, even after standing for some time. More dilute acid (strength about 87 per cent. SO^4H^2) forms β hexyl-sulphuric acid, which is capable of forming salts. *Acid chromate of potassium* and dilute sulphuric acid convert it into an aldehyde, which has no tendency to take up oxygen from the air, and when further oxidised with the same oxidising agent, yields, not caproic acid, but carbonic acid, water, butyric and acetic acids. The β variety of the alcohol has not been converted into the α variety; on the contrary, there is every reason to believe that the two bodies are radically different. (Wanklyn and Erlenmeyer, Chem. Soc. J. xvi. 221.)

Hexyl-aldehydes.—*a Hexyl-aldehyde*, *a* $C^6H^{12}O$.—Unknown: it might perhaps be obtained by oxidation from the *a* alcohol of fusel-oil, or of that derived from the hexyl-hydride found in petroleum.

β Hexyl-aldehyde, *β* $C^6H^{12}O$.—Obtained by oxidising the corresponding alcohol with acid chromate of potassium and dilute sulphuric acid. It is a colourless limpid liquid of fragrant penetrating odour; boils at 127° (bar. = 761·2 millimetres). Specific gravity at 0° = 0·8298, at 50° = 0·7846: coefficient of expansion between 0° and 50° = 0·0576. It forms a solid compound with acid sulphite of sodium; does not reduce ammonio-nitrate of silver; does not take up oxygen from the air. 100 parts of water dissolve about one part of *β* hexyl-aldehyde. When treated with *acid chromate of potassium* and dilute sulphuric acid, it yields no caproic acid, but butyric, acetic, and carbonic acids, and water (Wanklyn and Erlenmeyer, Chem. Soc. J. xvi. 307). A consideration of these reactions of *β* hexylic aldehyde leads to the conclusion that it is an acetone; for whilst the aldehydes take up oxygen from the air and yield by oxidation the corresponding acid, the acetones do not take up oxygen from the air, and yield lower acids (when oxidation is brought about).

This view of the case becomes increasingly probable when the history of acetic acetone, lately brought to light by Lieben, is considered. Acetone is reduced by hydrogen to tritylic alcohol; but the tritylic alcohol thus formed yields by oxidation, not propionic aldehyde, but common acetone.

β Hexyl-aldehyde will probably turn out to be either methyl-valeryl, $\left.\begin{matrix}CH^3\\C^5H^9O\end{matrix}\right\}$, or ethyl-butyryl, $\left.\begin{matrix}C^2H^5\\C^4H^7O\end{matrix}\right\}$.

Chlorides of Hexyl.—*a Hexyl-chloride*, *a* $C^6H^{13}Cl$, is obtained by Pelouze and Cahours, by the action of chlorine upon the hydride of hexyl existing in American petroleum. In addition to the *a* chloride of hexyl, further substitution-products are obtained. *a* Chloride of hexyl decomposes an alcoholic solution of *monosulphide of potassium*, giving *a* sulphide of hexyl, *a* $(C^6H^{13})^2S$, boiling at 230°. With *sulphydrate of potassium*, it gives hexyl-mercaptan: boiling point 145° to 148°. With *cyanide of potassium*, it seems to give *a* cyanide of hexyl. (Compt. rend. x. 1241, *et seq.*)

β Hexyl-chloride is obtained by saturating the corresponding alcohol with dry hydrochloric acid, and heating in the water-bath under pressure. It is an oily liquid, lighter than water, boiling at about 120°, and yielding hexylene when digested at 100° with alcoholic solution of potash.

Hydrides of Hexyl.—*a Hexyl-hydride*, *a* C^6H^{14}, was found by Greville Williams in the products of the distillation of Boghead coal, and called by him (originally) propyl (with which it is isomeric); in 1862 he came to the conclusion that his propyl was hexyl-hydride (Chem. Soc. J. xv. 130). Pelouze and Cahours found the same substance in American petroleum (Compt. rend. liv. 1241), and obtained a chlorine substitution-product from it, which reacted as chloride of hexyl should do. From the chloride was indirectly obtained an alcohol (p. 152) boiling at about 150°, and like amyl-alcohol in odour. Schorlemmer obtained the hydride also from the products of distillation of Cannel coal. Its boiling point is 68°. Density of the liquid = 0·6745 at 18° (Williams); 0·669 at 16° (Pelouze and Cahours); 0·678 at 15·5° (Schorlemmer). The vapour-density corresponds closely with the formula C^6H^{14}. It is a colourless mobile liquid, having a fragrant odour. Chemically, like all bodies of its class, it is very inactive. Neither sulphuric acid nor nitric acid attacks it; chlorine and bromine only with difficulty. In the arts, a mixture of *a* hydride of hexyl with other hydrides goes by the name of *turpentine substitute*.

β Hexyl-hydride, *β* C^6H^{14}, is obtained indirectly from mannite. It may be prepared by digesting zinc with *β* iodide of hexyl and water or alcohol; or by exposing mercury and the iodide to the action of sunlight. In the latter case the reaction is:

$$Hhg + 2C^6H^{13}I = HhgI^2 + C^6H^{12} + C^6H^{14}.$$

In the former case hexylene also accompanies the hydride. In order to remove the hexylene, it is well to shake up with sulphuric acid, which enters into combination with the hexylene.

In smell, boiling point, and outward appearance, the *β* hydride resembles the *a* hydride very closely. In specific gravity, however, it appears to differ from the *a* compound, being lighter. At 16·5° its specific gravity does not exceed 0·6645. Its derivatives are probably quite distinct from those of the *a* hydride.

Iodides of Hexyl.—*a Hexyl-iodide*, *a* $C^6H^{13}I$, is obtained by Pelouze and Cahours from hydride of hexyl existing in American petroleum. It boils at 172° to 175° (being of higher boiling point than the *β* iodide), and smells like iodide of amyl. It is acted upon by light. It reacts with a variety of salts, forming ethers. The alcohol which is indirectly obtained from it boils at 150°, and is believed by Pelouze and Cahours to be identical with Faget's alcohol extracted from fusel-oil (Compt. rend. liv. 1241, *et. seq.*) Wurtz has also obtained a hexyl-iodide by acting with hydriodic acid upon a variety of hexylene which seems to be distinct from the β hexylene of mannite.

β *Hexyl-iodide* is prepared by boiling mannite with a great excess of the strongest aqueous solution of hydriodic acid in a stream of carbonic anhydride (24 grms. mannite to 300 cub. cent. of acid, boiling at 126° C.); phosphorus may be added to the boiling liquid with great advantage. The iodide of hexyl appears in the form of an oily distillate, which should be freed from iodine and purified by distilling it in contact with water. When the operation is properly performed, very nearly the theoretical quantity of perfectly pure iodide of hexyl is obtained. The change which takes place is represented by:

$$\underset{\text{Mannite.}}{C^6H^8(HO)^6} + 11\,HI = \underset{\text{Iod hexyl.}}{C^6H^{13}I} + 6H^2O + I^{10}.$$

Melampyrin (ii. 349) may be substituted for mannite in the above process; but the yield is not so good. The β iodide may also be prepared by digesting β hexylene with hydriodic acid.

β Iodide of hexyl is a colourless liquid, not to be distinguished by the smell from iodide of amyl. Specific gravity at 0° = 1·4447; at 50° = 1·3812; its co-efficient of expansion between 0° and 50° is 0·0460. The boiling point at 752 millimetres = 167·5° C. It is only very slightly decomposed by distillation, and is, on the whole, a very stable compound.

The almost invariable product of the reaction of this iodide is hexylene. With alcoholic solution of potash, it has given very nearly the theoretical quantity of hexylene:

$$\beta\, C^6H^{13}I + KHO = \beta\, C^6H^{12} + H^2O + KI.$$

With *oxide of silver* and water, *acetate of lead*, *mercury*, *sodium*, *oxalate of silver*, *zinc and water*, or *zinc and alcohol*, and finally, when heated to 190° with *water* alone, it invariably yields considerable quantities of hexylene, other products being formed at the same time, according to the reagent employed.

Bromine acts with great violence, replacing the equivalent of iodine in β iodide of hexyl.

β **Hexyl-oxide,** $\beta \left.\begin{matrix}C^6H^{13}\\C^6H^{13}\end{matrix}\right\}O$ is formed, together with the olefine and alcohol, when moist oxide of silver acts upon the corresponding iodide:

$$Ag^2O + 2\,\beta\, C^6H^{13}I = 2AgI + \beta \left.\begin{matrix}C^6H^{13}\\C^6H^{13}\end{matrix}\right\}O.$$

It is a thick, slightly yellow liquid, not miscible with water, and of a faint penetrating smell. Boils constantly between 203·5° and 208·5°, with the barometer at 751 millimetres.

Hexyl-sulphuric acids. — α *Hexyl-sulphuric acid*, $\alpha \left.\begin{matrix}C^6H^{13}\\H\end{matrix}\right\}SO^4$, is little known.

β *Hexyl-sulphuric acid* is obtained by the action of sulphuric acid (diluted with about one-third of its volume of water) either on β hexylene, or on β hexyl-alcohol. It is partially decomposed by dilution with water, and gives off β hexyl-alcohol. Salts of this acid have been obtained.

β **Sulphydrate of Hexyl,** or β *Hexyl-mercaptan*, is obtained by digesting the β iodide with a concentrated alcoholic solution of sulphydrate of potassium:

$$\beta\, C^6H^{13}I + KHS = \beta \left.\begin{matrix}C^6H^{13}\\H\end{matrix}\right\}S + KI.$$

On adding water to the product of the reaction, the mercaptan separates as a clear, colourless, mobile liquid, not miscible with water and lighter than water. β Hexyl-mercaptan is formed *in the theoretical quantity* in this operation. As was mentioned above, an alcoholic solution of hydrate of potassium transforms β iodide of hexyl almost completely into hexylene and water; sulphydrate of potassium, on the other hand, transforms the iodide into β sulphydrate of hexyl. When an alcoholic solution of *sulphide of potassium* is used, there is also no formation of hexylene, but of a β sulphide instead, so that the sulphur-compounds of the β series are much more stable than the corresponding oxygen-compounds.

It is further noteworthy that β hexyl-mercaptan boils at 142° under a bar. pressure of 760 millimetres—being the point at which the α mercaptan ought to boil.

β Hexyl-mercaptan has the kind of smell characteristic of a mercaptan, only it seems not to be so persistent as the smell of common mercaptan. It acts upon oxide of mercury with energy. Sodium attacks it, with evolution of a gas and formation of a white residue; no doubt the reaction is of the usual kind:

$$\left.\begin{matrix}\beta\ C^6H^{13}\\ H\end{matrix}\right\}S + Na = \left.\begin{matrix}\beta\ C^6H^{13}\\ Na\end{matrix}\right\}S + H.$$

Very curiously, caustic potash, both solid and in aqueous solution, also attacks this mercaptan; and, still more curiously, a heat of 100° C. decomposes the compound formed with aqueous potash, occasioning separation of the mercaptan, which, however, recombines on cooling. J. A. W.

HEXYLENE. C^6H^{12}.—Of this hydrocarbon there are also two modifications.

α Hexylene. It is doubtful whether Fremy's hydrocarbon, boiling at 55° and obtained by the distillation of hydroleic and metoleic acids, was hexylene. Greville Williams obtained hexylene from the products of the distillation of Boghead coal. It boiled at 71° (Phil. Trans. 1847). Wurtz seems to have obtained a variety of hexylene from fusel-oil.

β Hexylene is formed by the reaction of the corresponding iodide with most reagents. It is best prepared by the action of the iodide upon alcoholic solution of caustic potash, at 100°. In preparing it, the precaution should be taken to distil the alcoholic solution of hexylene from the iodide of potassium produced during the reaction, and to digest the distillate with fresh potash. The alcohol is subsequently removed by washing.

β Hexylene is a very mobile liquid, lighter than, and not miscible with, water. Boiling point 68° to 70°. Its odour is very unpleasant, just like that of amylene. Vapour-density, by experiment, 2·88 and 2·97 (theory requires 2·9022). It combines with *bromine* with great violence, forming $C^6H^{12}Br^2$. With concentrated *sulphuric acid* it gives parahexylene. With sulphuric acid diluted with about one-third its volume of water, it gives β hexyl-sulphuric acid. β Hexylene seems to be a lighter liquid than α hexylene. J. A. W.

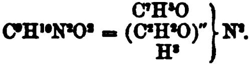
HIPPARAFFIN. C^8H^7NO.—A product of the oxidation of hippuric acid, discovered by Schwarz (Ann. Ch. Pharm. lxxv. 201), further investigated by J. Maier, (*ibid.* cxxvii. 161), who has shown that hipparin is formed at the same time. To prepare it, hippuric acid is stirred up to a paste with dilute sulphuric acid, then mixed with peroxide of lead, and left to stand at a gentle heat for 12 to 24 hours. The mass is then washed with cold water; the residue exhausted with alcohol; the alcoholic solution evaporated; the residue washed with carbonate of soda to remove benzoic and undecomposed hippuric acid; and the residue boiled with water, which leaves hipparaffin undissolved and deposits hipparin on cooling. (Maier.)

Hipparaffin crystallises from hot alcohol in extremely soft slender needles, having a silky lustre and arranged in thick interlaced tufts. It has neither taste nor odour; dissolves sparingly in hot, and is quite insoluble in cold *water*, which does not even wet it; the solubility is not increased by addition of sulphuric acid, hydrochloric acid, ammonia or potash. It dissolves in strong *sulphuric acid*, and is precipitated by water without much alteration (Schwarz). Dissolves easily in strong sulphuric and nitric acid, and is not precipitated from either solution by water (Maier). It dissolves readily in boiling *alcohol*, and very readily in *ether*. It melts at 200° (Schwarz), 210° (Maier), solidifying in the crystalline form as it cools. At a higher temperature part of it distils without alteration, the residue turning black (Schwarz); a small quantity sublimes in slender needles even below 100°. (Maier.)

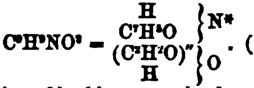
Hipparaffin burns with a bright smoky flame, leaving a small quantity of easily combustible charcoal. It is not decomposed by solution of *iodine*, or by *hydrochloric acid and chlorate of potassium*, or by aqueous *chromic acid*. It is but partially decomposed by fusion with *hydrate of potassium;* but on igniting it with *potash-lime*, benzene is produced, and the whole of the nitrogen is given off in the form of ammonia (Schwarz). Heated to 200°—220° in a stream of *hydrochloric acid gas*, it gives off a colourless oil, which solidifies in the crystalline form. *Fuming nitric acid* dissolves it, with evolution of gas, and the solution, concentrated after neutralisation with soda, yields a precipitate of benzoic acid. Heated with *peroxide of lead* and dilute sulphuric acid, it gives off all its carbon in the form of carbonic anhydride. (Schwarz.)

HIPPARIN. $C^8H^7NO^2$. (J. Maier, *loc. cit.*)—The preparation is given in the preceding article. Hipparin crystallises in large silky needles united in barrel-shaped groups. Melts at 45·7°; solidifies at about 20°; burns with a bright flame; dissolves easily in alcohol, ether, and boiling water.

HIPPOPHAË RHAMNOIDËS. The *Sea Buckthorn.*—This plant contains a yellow colouring matter which appears to be identical with quercitrin. It is obtained by exhausting the berries, after they have been well boiled in water and dried, with hot alcohol; mixing the hot filtered liquid with basic acetate of lead; decomposing the precipitate with sulphydric acid; heating the whole; filtering when cold; and treating the precipitated sulphide of lead with hot alcohol. The colouring matter then dissolves, and remains on evaporation, as a brown-red brittle mass still retaining a little fat, from which it may be purified by treatment with ether, absolute alcohol, &c. It is then obtained as a yellow mass containing rudimentary crystals. The berries likewise contain oxalic and malic acids, a peculiar fat, &c., which are extracted by boiling them with water. (Bolley, Dingl. pol. J. clxii. 143; Jahresber. 1861, p. 708.)



HIPPURAMIDE. $C^9H^{10}N^2O^2 = \left.\begin{matrix}C^7H^5O\\(C^2H^2O)''\\H^2\end{matrix}\right\}N^2$.—This amide is produced by the prolonged action of ammonia on an alcoholic solution of hippurate of methyl, and remains when the solution is evaporated. It dissolves in 100 pts. water at ordinary temperatures, in 80 pts. wood-spirit, and 50 pts. alcohol; sparingly soluble in ether. By alkalis at the boiling heat it is resolved into ammonia and hippuric acid. (Jacquemin and Schlagdenhauffen, Compt. rend. xlv. 1011.)



HIPPURIC ACID. $C^9H^9NO^3 = \begin{array}{c}H\\C^7H^5O\\(C^2H^2O)''\\H\end{array}\begin{array}{l}\left.\vphantom{\begin{matrix}H\\C\end{matrix}}\right\}N^*\\\left.\vphantom{\begin{matrix}H\\C\end{matrix}}\right\}O\end{array}$. (Gm. xii. 69; Gerh. iii. 242).—This acid exists in the urine of herbivorous animals, and in smaller quantity in that of man. Rouelle, towards the end of the last century, first observed that the urine of horses contained an acid bearing considerable resemblance to benzoic acid, and the observation was afterwards confirmed by Fourcroy and Vauquelin, who separated the acid by addition of hydrochloric acid; but its real nature and separate identity were first established by Liebig, in 1830 (Ann. Ch. Pharm. xii. 20). The urine of cows and horses does in fact contain, sometimes hippuric and sometimes benzoic acid, the former acid being easily converted into the latter by oxidation; and this change often taking place within the animal organism. When horses are kept in the stable, or only lightly worked, their urine contains hippuric acid; but when they are put to hard work, it contains benzoic acid.

Cows' urine, according to Boussingault, contains about 1·3 per cent. of hippuric acid; in that of horses, the maximum amount is about 0·38 per cent.; that of swine does not appear to contain hippuric acid; that of the camel and elephant yields a considerable quantity.

From the experiments of Henneberg, Stohmann, and Rautenberg (Ann. Ch. Pharm. cxxiv. 181; Rép. Chim. pure 1863, p. 223; Jahresber. 1862, p. 541) it appears that the urine of oxen contains a maximum quantity of hippuric acid (2·1 to 2·7 per cent.) when the animals are fed on oat- and wheat-straw with a small admixture of beans. The straw and dried herb of leguminous plants reduced the amount to 0·4 per cent. With the hay of graminaceous plants intermediate results were obtained. The addition of a certain quantity of beans, starch, sugar, or oil, diminished the proportion of hippuric acid, and increased that of urea.

In human urine, the proportion of hippuric acid is but small under normal conditions, and about equal to that of uric acid (Liebig; Bence Jones); in certain diseases, as in diabetes, according to Lehmann, the amount is considerably greater; a vegetable diet likewise increases it. In the urine of a healthy man living on a mixed diet, Bence Jones (Chem. Soc. J. xv. 81) found, by Liebig's method of estimation (p. 158), from 0·03 to 0·04 per cent. hippuric acid; Thudichum (*loc. cit.* xvii. 55) found the same quantity under similar circumstances; but the amount was largely increased by eating greengages. Weismann (J. pr. Chem. lxxiv. 106; Jahresber. 1858, p. 572) and Wreden (J. pr. Chem. lxxvii. 146; Jahresber. 1859, p. 700) found much larger quantities; but the former appears to have operated on too small a quantity of urine, and the latter adopted a defective method of analysis (p. 159).

Formation.—1. By heating glycocine in a sealed tube with benzoic acid:

$$C^2H^5NO^2 + C^7H^6O^2 = C^9H^9NO^3 + H^2O;$$

also by heating the zinc-salt of glycocine with chloride of benzoyl to 120° in a sealed tube, or by simply leaving the two compounds in contact for some time:

$$C^2H^4ZnNO^2 + C^7H^5OCl = C^9H^9NO^3 + ZnCl.$$

This formation of hippuric from benzoic acid likewise takes place when the latter acid is injected into the blood of a living animal, together with glycocine or glycocholate of sodium, or bile. When about 2 grms. of benzoic acid, and 30 c.c. of bile free from mucus were injected into the blood of a dog or cat, the urine was found to contain a considerable quantity of hippuric, but no benzoic acid; with a larger proportion of benzoic acid, the excess passed into the urine together with the hippuric acid. Benzoic acid injected into the circulation alone, is not converted into hippuric acid. (**Kühne** and **Hallwachs**, Jahresber. 1859, p. 638.)

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* On the rational formula of hippuric acid, see FORMULÆ (ii. 697).

2. Benzoic acid is likewise converted into hippuric acid in the animal organism when introduced into the alimentary canal, hippuric acid being found in the urine after benzoic acid has been swallowed. Marchand, after taking 30 grains of benzoic acid, found 39·2 grs. of hippuric acid in his urine (by calculation, it should have been 44 grs.). Similar observations have been made by **Al. Ure** (J. Pharm. xxvii. 646), **Keller** (Ann. Ch. Pharm. xliii. 198), and **Garrod** (Phil. Mag. [3] xx. 501).

3. Quinic acid is also converted in the animal organism into hippuric acid (probably first into benzoic acid). When 8 grms. of quinate of calcium were swallowed over night, the morning urine was found to contain 2 grms. of hippuric acid. (**Lautemann**, Ann. Ch. Pharm. cxxv. 9.)

Preparation from horses' or cows' urine.—Hippuric acid exists in the urine in combination with ammonia. To obtain it, the fresh urine of cows or of horses which have been kept at rest, is concentrated by evaporation to $\frac{1}{8}$ or $\frac{1}{6}$ of its bulk and supersaturated with hydrochloric acid; it then, after a while, deposits a yellowish-brown precipitate of hippuric acid.

The evaporation of the urine, which is tedious, may be obviated by mixing it with a considerable excess of hydrochloric acid, the solubility of the hippuric acid being thereby greatly diminished. 100 pts. of cows' urine mixed with 2 or 3 pts. of crude hydrochloric acid soon deposits hippuric acid (**Riley**, Chem. Soc. Qu. J. v. 97). Another mode of expediting the process is to mix the fresh urine with milk of lime, boil for a few minutes and strain; then evaporate the solution of hippurate of calcium to $\frac{1}{6}$ or $\frac{1}{12}$ of its bulk, according to the previous concentration; and supersaturate with hydrochloric acid. (**Gregory**, Ann. Ch. Pharm. lviii. 125.)

The acid obtained as above has a brownish colour and disagreeable urinous odour, and requires further purification. This may be effected in several ways: 1. **Schwarz** (Ann. Ch. Pharm. liv. 29) boils the crude acid with milk of lime, which removes the greater part of the fibrin with which it is contaminated; precipitates the filtrate with carbonate of sodium, then boils and filters again, and mixes the filtrate with solution of chloride of calcium, the carbonate of calcium thereby precipitated carrying down the colouring matter; then filters a third time, and precipitates with hydrochloric acid. The hippuric acid thus purified is quite colourless.—2. The crude acid, mixed with 10 pts. of boiling water and excess of milk of lime, is submitted to pressure; the expressed liquid is mixed with solution of alum till it no longer exhibits an alkaline reaction, and left to cool to 40°; carbonate of sodium is then added as long as a precipitate continues to form; and the liquid is again separated by straining and pressure, and precipitated by hydrochloric acid: the hippuric acid thus obtained is washed with cold water, pressed and dissolved in boiling water, and the solution is mixed with blood-charcoal (1 oz. to a lb. of the acid), filtered through paper while still at the boiling heat, and left to crystallise (**Bensch**, Ann. Ch. Pharm. lviii. 267).—3. **Löwe** prepares hippuric acid by mixing fresh horse-urine with excess of sulphate of zinc; evaporating the liquid together with the precipitate to $\frac{1}{6}$ or $\frac{1}{8}$ of its bulk; filtering quickly; washing the precipitate with a small quantity of hot water; and decomposing the hippurate of zinc in the filtrate with dilute sulphuric or hydrochloric acid. Hippuric acid then separates in the form of a white magma, which may be washed with cold water, pressed between paper, and recrystallised from boiling water. The addition of sulphate of zinc to the urine preserves it from putrefaction, and enables the experimenter to wait till a considerable quantity is collected.

Properties.—Hippuric acid forms colourless transparent prisms, having an unctuous adamantine lustre, and often of considerable size. The crystals belong to the trimetric system. Ordinary combination, $\infty P . \bar{P}\infty . \breve{P}\infty$. with the modifying faces $\infty\breve{P}\infty$ and $\infty\bar{P}\infty$. Ratio of the axes, $a : b : c = 0·9742 : 1·1606 : 1$. Inclination of the faces: $\infty P : \infty P$ in the brachydiagonal principal section = 99° 59′; $\breve{P}\infty : \breve{P}\infty$ = 98° 30′; $\bar{P}\infty : \bar{P}\infty$ in the macrodiagonal principal section = 88° 30′. Cleavage tolerably easy, parallel to oP. Specific gravity = 1·308. Hippuric acid melts at a gentle heat, and solidifies in a crystalline mass on cooling. It has a slightly bitter taste, and reddens litmus strongly. It is sparingly soluble in cold *water*, 1 pt. of the crystals requiring 600 pts. of water at 0°. Boiling water and *alcohol* dissolve it readily; *ether* scarcely at all. Hippuric acid likewise dissolves, but very sparingly, in water containing *hydrochloric acid*. It dissolves with the greatest facility in water containing ordinary *phosphate of sodium*, in such quantity indeed as to change the reaction of the solution from alkaline to acid—a property which is also possessed by uric acid. This, according to Liebig, is the cause of the acid reaction exhibited by the urine of man and other animals in the recent state.

Decompositions.—1. Hippuric acid boils at 240°, yielding a crystalline product, consisting in great part of benzoic acid and benzonitrile (cyanide of phenyl); a strong odour of hydrocyanic acid is likewise evolved, and a considerable quantity of charcoal remains in the retort. Dry hippuric acid, heated in a retort with dry chloride of zinc and quartz-sand, yields benzonitrile, carbonic anhydride, and charcoal (**Gössmann**, Ann. Ch. Pharm. c. 69):

$$2C^9H^9NO^3 - 4H^2O = 2C^7H^5N + CO^2 + C^3.$$

2. Hippuric acid in alkaline solution is slowly oxidised by *ozone*, with formation of carbonic acid and a small quantity of formic acid (**Gorup-Besanez**, Ann. Ch. Pharm. cxxv. 217).—3. Pure hippuric acid is not altered by boiling with *water;* but when horse-urine is quickly evaporated, ammonia is given off, and the hippuric acid contained in it is converted into benzoic acid. Cows' urine does not yield benzoic acid when boiled.—4. Hippuric acid dissolves in strong *hydrochloric acid* at the boiling heat, and on continuing the ebullition, it is resolved into benzoic acid and glycocine:

$$\underset{\text{Hippuric acid.}}{C^9H^9NO^3} + H^2O = \underset{\text{Glycocine.}}{C^2H^5NO^2} + \underset{\text{Benzoic acid.}}{C^7H^6O^2}.$$

The same decomposition is effected by boiling dilute *sulphuric acid*, by *nitric*, and even by *oxalic acid.*—5. Hippuric acid, boiled for half-an-hour with caustic *potash* or *soda*, is converted into glycocine and an alkaline benzoate. It is not decomposed by boiling with milk of lime.—6. The resolution of hippuric acid into benzoic acid and glycocine is likewise effected by the action of a *ferment* in presence of an alkali (**Buchner**, Ann. Ch. Pharm. lxxviii. 203).—7. By the action of *nascent hydrogen*, it appears to be resolved into hydride of benzoyl and glycocine (**Erlenmeyer**, Zeitschr. Ch. Pharm. 1861, p. 548).—8. *Nitrous acid* converts hippuric acid into benzoglycollic acid, with evolution of nitrogen gas:

$$2C^9H^9NO^3 + N^2O^3 = 2C^9H^8O^4 + H^2O + N^4.$$

This decomposition takes place when nitric oxide is passed into a solution of hippuric acid in nitric acid.—9. A cold mixture of strong *sulphuric acid* and fuming *nitric acid* converts hippuric acid into nitrohippuric acid. With *sulphuric anhydride*, it unites directly, forming sulphohippuric acid, $C^9H^9NSO^6$.—10. An aqueous solution of hippuric acid is not decomposed by *chlorine* gas; but on boiling it with a large excess of *bleaching powder*, decomposition takes place (**Liebig**). When chlorine is passed into a solution of hippuric acid in rather dilute potash, nitrogen is evolved, and benzoglycollic acid is produced (**Gössmann**):

$$C^9H^9NO^3 + 3KHO + Cl^3 = C^9H^8O^4 + 2H^2O + 3KCl + N.$$

11. By mixing it with *hydrochloric acid*, and adding *chlorate of potassium* by small portions, it is converted into a mixture of monochlorohippuric acid, $C^9H^8ClNO^3$, and dichlorohippuric acid, $C^9H^7Cl^2NO^3$ (**R. Otto**, Ann. Ch. Pharm. cxxii. 129).—12. When hippuric acid is gently heated with 1 at. *pentachloride of phosphorus*, oxychloride of phosphorus and hydrochloric acid are given off, and a brown residue is left, soluble in alcohol and in ammonia, and precipitated therefrom in the resinous state by hydrochloric acid; but on distilling 1 at. hippuric acid with 2 at. pentachloride of phosphorus, the products obtained are oxychloride of phosphorus, chloride of benzoyl, and two chlorinated compounds, $C^9H^6ClNO^2$, and $C^9H^5Cl^2NO^2$, differing from mono- and dichlorohippuric acids respectively by 1 at. H^2O (**Schwanert**, see p. 161).—13. When hippuric acid is boiled with *peroxide of manganese* and very dilute sulphuric acid, a large quantity of carbonic anhydride is evolved, benzoic acid separates on cooling, and the liquid is found to contain sulphate of ammonium.—14. Hippuric acid, boiled with *peroxide of lead* and water, yields benzamide, water, and carbonic anhydride (**Fehling**):

$$C^9H^9NO^3 + 3O = C^7H^7NO + H^2O + 2CO^2.$$

When hippuric acid is heated with peroxide of lead and excess of nitric or sulphuric acid, the products formed are carbonic anhydride and hipparaffin (p. 154); but when it is boiled with water and peroxide of lead, and sulphuric acid added in quantity only sufficient to decompose the resulting hippurate of lead, the only product obtained is benzamide (**Schwartz**).—15. Hippuric acid, gently heated with excess of caustic *baryta*, yields a liquid which smells of benzene (no ammonia is evolved), is converted into crystalline scales by contact with hydrochloric acid, and, when distilled, yields pure benzene (**Gerhardt**). This liquid is perhaps benzonitrile.

Estimation of Hippuric acid in urine.—1. The urine is evaporated to a syrupy consistence over a water-bath; hydrochloric acid is added; and the hippuric acid is extracted by treating the precipitate four or five times with ether (**Liebig**, Ann. Ch. Pharm. l. 170). According to **Bence Jones** (Chem. Soc. J. xv. 81), this method gives exact results, provided sufficient urine is taken (about 400 c. c.), and a sufficient quantity of ether is used. **Thudichum** (Chem. Soc. J. xvii. 55) evaporates the urine to a stiff syrup, pours it into a bottle while yet warm, taking up the last residues with the necessary amount of hydrochloric acid; and shakes up the whole briskly with large quantities of dry ether. The ethereal solution is then distilled, the reddish yellow residue mixed with a little water, and allowed to crystallise; and the crystals of hippuric acid thus obtained are washed with water till the washings are colourless, then dried by pressure between blotting paper, afterwards by placing them over sulphuric acid, and finally at 100° in a water-oven. (See also Weismann, J. pr. Chem. lxxiv. 106; Jahresber. 1857, p. 637.)

2. Wreden (J. pr. Chem. lxxvii. 446; Jahresber. 1859, p. 700) estimates hippuric acid in urine by means of a standard solution of ferric chloride. The liquid is first neutralised and freed from phosphoric acid by means of baryta-water, and the iron solution is added till it no longer forms a precipitate, and a drop of the filtered solution produces a blue colour on a piece of filtering paper moistened with ferrocyanide of potassium. The amount of hippuric acid found in human urine by this method of estimation (average 0·38 per cent.) is much higher than that determined by Liebig's method (p. 156); and, according to Henneberg, Stohmann, and Rautenberg (Ann. Ch. Pharm. cxxiv. 181), the results are vitiated by the fact that a perfectly neutral solution of ferric chloride is decomposed by paper-fibre to such an extent, that paper soaked in a solution of yellow prussiate will not indicate the presence of a small quantity of iron; also, because the termination of the reaction cannot be distinctly perceived. Better results are obtained with ferric nitrate, after the urine has been freed from colouring matter and other bodies by nitrate of lead; but even in this case the process is sometimes rendered uncertain by the presence of other substances which exert a reducing action on the ferric oxide. Altogether, the mode of estimation by means of hydrochloric acid and ether appears to give the best results.

Hippurates. Hippuric acid is monobasic, the general formula of its salts being $C^9H^8MNO^3$. Most metallic oxides dissolve readily in the acid. The hippurates of potassium, sodium, ammonium and magnesium are very soluble and difficult to crystallise; their solutions form a cream-coloured precipitate with ferric salts, and white curdy precipitates with nitrate of silver and mercurous nitrate. A characteristic reaction of the hippurates is, that when fused with excess of potash or lime, they give off ammonia and yield benzene by distillation. Mineral acids decompose them, separating the hippuric acid.

Hippurate of Ammonium.—The *neutral salt* does not appear to exist. *An acid* salt, $C^9H^8(NH^4)NO^3.C^9H^9NO^3.H^2O$, is produced even when hippuric acid is mixed with excess of ammonia. It crystallises by concentration in square-based prisms with 4-sided summits. It dissolves in small quantities of water and alcohol, sparingly in ether, and performs gyratory movements when thrown on the surface of water.

Hippurate of Barium, $2C^9H^8BaNO^3 + H^2O$, forms prisms with rectangular base; soluble in water. It unites with benzoate of barium, forming a salt containing $2(C^9H^8BaNO^3.C^7H^5BaO^2).5H^2O$.

Hippurate of Calcium, $2C^9H^8CaNO^3.3H^2O$, crystallises sometimes in rectangular prisms, sometimes in laminæ. Specific gravity 1·318. It is soluble in 18 pts. of cold and 6 pts. of hot water.

Hippurate of Cobalt, $2C^9H^8CoNO^3.5H^2O$, forms rose-coloured needles or nodules, which give off their water at 100°.

Hippurate of Copper, $2C^9H^8CuNO^3.3H^2O$, obtained by concentrating a mixture of sulphate of copper and hippurate of potassium, forms oblique rhomboïdal prisms of an azure-blue colour, which turn green and give off their water of crystallisation when heated on the water-bath.

Hippurate of Iron (*ferricum*) is precipitated on mixing the concentrated solutions of hippurate of potassium and ferric chloride.

Hippurate of Lead, $C^9H^8PbNO^3 + H^2O$ and $+ \frac{3}{2}H^2O$, is obtained by precipitating a cold solution of neutral acetate of lead with hippurate of potassium, as a curdy precipitate which dissolves but slowly in boiling water. If the boiling solution is well diluted, the salt is deposited in silky needles (containing 1 at. water) grouped in tufts; but these crystals, even while immersed in the solution, are quickly converted into rather broad, shining laminæ ($\frac{3}{2}$ H^2O) having the form of quadrangular tables. The whole of the water is given off at 100°.

Hippurate of Magnesium, $2C^9H^8MgNO^3.5H^2O$, forms white nodules, which are soluble in water and give off $2H^2O$ at 100°.

Hippurate of Nickel, $2C^9H^8NiNO^3.5H^2O$, is crystallisable, insoluble in ether, sparingly soluble in cold water, more soluble in boiling water and in boiling alcohol. It becomes anhydrous at 100°.

Hippurate of Potassium.—The *neutral* salt, $C^9H^8KNO^3.H^2O$, forms oblique prisms with rhomboïdal base, soluble in water and in alcohol, and becoming anhydrous by desiccation at 100°. To obtain it pure, it must be crystallised several times from alcohol and washed with ether.

The *acid* salt, $C^9H^8KNO^3.C^9H^9NO^3.H^2O$, forms brilliant laminæ, which under the microscope are seen to consist of prisms with rectangular base, and the terminal edges truncated. They give off 4·77 per cent. water at 100°.

Hippurate of Silver, $2C^9H^8AgNO^3.H^2O$, prepared by adding nitrate of silver to hippurate of potassium, is soluble in water and crystallisable. It gives off its water (3·42 per cent.) at 100°.

Hippurate of Sodium, $2C^9H^8NaNO^3.H^2O$, is crystallisable, very soluble in hot water and in alcohol, sparingly in ether.

Hippurate of Strontium, $2C^9H^8SrNO^3.5H^2O$, is crystallisable; sparingly soluble in cold water and alcohol; gives off its water at 100°.

Derivatives of Hippuric Acid.

Amido-hippuric acid. $C^9H^{10}N^2O^3 = C^9H^8(NH^2)NO^3$. (Schwanert, Ann. Ch. Pharm. cxii. 69.)—Obtained by passing sulphydric acid gas for a considerable time into a solution of nitrohippuric acid in saturated sulphide of ammonium, and acidulating the concentrated liquid with hydrochloric, or better with nitric acid. It crystallises in light white laminæ, soluble in 300 to 370 pts. water at 20°, in 1200 pts. absolute alcohol at 15°, insoluble in ether. In boiling water and alcohol it dissolves easily; likewise in acids and in alkalis; the solutions quickly turn brown. With concentrated hydrochloric acid, it forms a *hydrochlorate* containing $C^9H^{10}N^2O^3.HCl$.

Chlorohippuric acids. (R. Otto, Ann. Ch. Pharm. cxxii. 129.)—These compounds are produced by the action of hypochlorous acid on hippuric acid. When 2 or 3 pts. chlorate of potassium are added to a mixture of 1 pt. hippuric acid and 6 to 9 pts. hydrochloric acid, a gentle heat applied, after the frothing has ceased, to complete the reaction, the liquid then heated to boiling and left to cool,—an oily yellowish mass is deposited, consisting of mono- and dichlorohippuric acids, their relative quantities depending, partly on the quantity of chlorate used, partly on the temperature of the liquid during the reaction. The two acids are separated, either by boiling with water, which dissolves chiefly the monochlorinated acid, or by repeated crystallisation of the calcium-salts obtained by neutralising the mixed acids with milk of lime.

Monochlorohippuric acid, $C^9H^8ClNO^3$, obtained by evaporating the alcoholic solution, after decolorisation with animal charcoal, forms a yellowish, viscid, inodorous mass, having an acid reaction; it is nearly insoluble in cold water, melts and dissolves in boiling water, and mixes in all proportions with alcohol and ether. It dissolves also in caustic alkalis, forming a solution which turns brown when heated.—By boiling with concentrated hydrochloric acid, it is resolved into glycocine and monochlorobenzoic acid.

The *neutral potassium-* and *sodium-salts*, are uncrystallisable or crystallise with difficulty. The *acid sodium-salt*, $2(C^9H^7ClNaNO^3.C^9H^8ClNO^3).H^2O$, crystallises in concentrically grouped needles.—The *calcium-salt*, $C^9H^7ClCaNO^3.2H^2O$, crystallises from alcohol in small shining scales.—The *lead-salt*, $C^9H^7ClPbNO^3$, melts at 100—120°, and crystallises from dilute alcohol in concentrically grouped needles.—The *silver-salt* is a white precipitate, which crystallises indistinctly from solution in water.

Dichlorohippuric acid, $C^9H^7Cl^2NO^3$, is very much like the monochlorinated acid, and after standing in contact with the air or under water, forms a soft granulo-crystalline mass, which deliquesces when warmed, and at 60° emits an aromatic turpentine-like odour.—By boiling with strong hydrochloric acid, it is resolved into glycocine and dichlorobenzoic acid.

Dichlorohippurate of sodium, $C^9H^6Cl^2NaNO^3.H^2O$, forms soft warty crystals, easily soluble in water, alcohol, and acids.—The *barium-salt*, $2C^9H^6Cl^2BaNO^3.3H^2O$, crystallises in needles.—The *calcium-salt*, $C^9H^6Cl^2CaNO^3$, crystallises from dilute solutions at ordinary temperatures, or at 60°, in needles containing $4\frac{1}{2}$ or 5 at. water; at higher temperatures, in hard white crusts with $\frac{5}{2}$ at. water.—The *neutral lead-salt*, $C^9H^6Cl^2PbNO^3.2H^2O$, obtained by cold precipitation, separates from its aqueous solution in nodules. A *basic lead-salt*, $4C^9H^6Cl^2PbNO^3.Pb^2O.6H^2O$, may be extracted by boiling absolute alcohol from the precipitate formed from dichlorhippuric acid and acetate of lead at the boiling heat. The *silver-salt* is a white precipitate, which separates from hot water in cauliflower-like masses.

Dichlorohippurate of Ethyl, $C^9H^6Cl^2(C^2H^5)NO^3$, obtained by treating the alcoholic solution of the acid with hydrochloric acid gas, is a heavy yellowish oil, nearly insoluble in water.

A *calcium-salt* having the composition, $C^{18}H^{13}Ca^2Cl^3N^2O^6.5H^2O$, intermediate between the mono- and dichlorohippurates, is obtained in spherical groups of needles by crystallising a mixture of the calcium-salts of the two acids. Its solution precipitated by nitrate of silver yields a *silver-salt* of analogous composition.

Compounds produced by the action of Pentachloride of Phosphorus on Hippuric acid. (H. Schwanert, Ann. Ch. Pharm. cxii. 59.)—When 1 at. hippuric acid (in quantities not exceeding 10 grms.) is distilled with 2 at. pentachloride of phosphorus, scarcely anything but oxychloride of phosphorus passes over at first, but between 180° and 200° a viscid liquid distils over, and between 220° and 250° a mass which solidifies in the crystalline form. The liquid separated from the crystals gives off, on rectification, oxychloride of phosphorus up to 120°, then chloride of benzoyl, boiling at 196°, and an oil which boils at a temperature above 200°, and when left over oil of vitriol, solidifies to a crystalline mass whose composition is expressed by the formula, $C^9H^6ClNO^2 = C^9H^8ClNO^3$ (monochlorohippuric acid) − H^2O, which is also the composition of the crystals obtained by the first distillation.—This compound, when immersed in ether, deliquesces at a gentle heat to a yellowish oil, without perceptibly dissolving, and crystallises on cooling in flat four-sided monoclinic prisms bevelled at the ends with two faces. It melts between 40° and 50°, distils without alteration at 200°, is insoluble in water, but dissolves easily in alcohol, and crystallises therefrom with difficulty. The solution is not precipitated by chloride of platinum, mercuric chloride, or nitrate of silver. The compound is not decomposed by potash, either in aqueous or in alcoholic solution, but when repeatedly fused with hydrate of potassium, it is partially resolved into ammonia and benzoic acid; aqueous ammonia also decomposes it partially at 130°. It absorbs hydrochloric acid gas in quantity corresponding nearly with the formula, $C^9H^6ClNO^2.HCl$, but the hydrochlorate loses its acid, even when the alcoholic solution is evaporated over oil of vitriol.

Another chlorinated compound, $C^9H^5Cl^2NO^2 = C^9H^7Cl^2NO^3$ (dichlorohippuric acid) − H^2O, is obtained, though only in small quantity, by repeatedly rectifying the last portions of oil which pass over in distilling hippuric acid with pentachloride of phosphorus. It is likewise crystalline, but dissolves readily in ether.

Nitrohippuric acid. $C^9H^8N^2O^5 = C^9H^8(NO^2)NO^3$. (Bertagnini, Ann. Ch. Pharm. lxxviii. 100.)—This acid is produced by the action of a mixture of strong sulphuric and fuming nitric acid on hippuric acid. It is found in the urine after nitrobenzoic acid has been swallowed. To prepare it, 1 pt. of hippuric acid is dissolved, in the cold, in 4 pts. of the strongest nitric acid, and the solution is mixed, slowly, so as to avoid rise of temperature, with 4·9 pts. of strong sulphuric acid. The liquid is then left to itself for two hours, and diluted, still slowly, to avoid heating, with three times its volume of water; it then, after two hours, deposits an abundant crystallisation of nitrohippuric acid. The acid thus obtained has a yellow colour; for purification, it is treated with lime, the resulting calcium-salt is decomposed with hydrochloric acid, and the nitrohippuric acid is recrystallised several times.

Nitrohippuric acid crystallises in colourless silky needles, soluble in alcohol, ether, and water, especially in water containing phosphate of sodium. The crystals redden litmus, melt at about 150°, and then decompose, giving off vapours of benzoic acid.

Hydrochloric acid converts nitrohippuric acid into glycocine and nitrobenzoic acid. A solution of nitrohippuric acid mixed with *ammonia* assumes a red colour under the influence of *sulphydric acid*, and deposits sulphur when neutralised by an acid. When dissolved in a saturated solution of sulphide of ammonium, and treated with sulphydric acid, it is converted into amido-hippuric acid, $C^9H^{10}N^2O^3$ (Schwanert, p. 160). *Nitric oxide* passed into a solution of nitrohippuric acid in nitric acid gives rise to the formation of a new acid, not yet examined. Nitrohippuric acid dissolves at ordinary temperatures in strong *sulphuric acid*, and on gently heating the solution and then diluting with water, nitrobenzoic acid is deposited. Nitrohippuric acid distilled with an equal weight of *quick-lime* yields a reddish, oily distillate having the odour of cinnamon. The acid heated with strong solution of *potash*, turns brown and gives off ammonia: at a higher temperature, the mixture gives off hydrogen and assumes a red colour.

The nitrohippurates are mostly soluble in water, some of them also in alcohol. Most of them crystallise in needles grouped round a common centre. When heated, they give off aromatic vapours. The following have been analysed:

Calcium-salt	$2C^9H^7Ca(NO^2)NO^3.3H^2O$.
Cupric salt	$2C^9H^7Cu(NO^2)NO^3.5H^2O$.
Lead-salt	$C^9H^7Pb(NO^2)NO^3$ (at 110°).
Silver-salt	$C^9H^7Ag(NO^2)NO^3$.
Zinc-salt	$C^9H^7Zn(NO^2)NO^3.3H^2O$.

Sulphohippuric acid. $C^9H^9NSO^6 = C^9H^9NO^3.SO^3$. (Schwanert, Ann. Ch. Pharm. cxii. 59.)—Produced by direct combination. Hippuric acid absorbs the vapour of sulphuric anhydride, forming a brown liquid; and by dissolving this product in water, neutralising with carbonate of lead, decomposing the filtrate with sulphydric acid, and evaporating, sulphohippuric acid is obtained as a brownish yellow, amorphous, deliquescent mass.

With *nitrous acid* it forms (not sulphobenzoglycollic, but) sulphobenzoic acid, $C^7H^6SO^5$, together with an oily substance probably containing glycollic acid.

Sulphohippuric acid is dibasic. Its neutral *barium-salt* contains $C^9H^7Ba^2NSO^6.H^2O$. By boiling the acid with hydrate of lead, a *lead-salt* is obtained corresponding approximately with the formula $C^9H^7Pb^2NSO^6$.

HIPPURIC ETHERS. Only two of these compounds have as yet been obtained, viz. the ethylic and methylic ethers.

Hippurate of Ethyl. $C^{11}H^{13}NO^3 = C^9H^8(C^2H^5)NO^3$. (Stenhouse, Ann. Ch. Pharm. xxxi. 148.)—Prepared by passing hydrochloric acid gas through a boiling solution of hippuric acid in alcohol of 80 per cent. The liquid thickens, assumes an oily aspect, and when diluted with water, deposits the ether in liquid drops, which soon solidify.

Hippurate of ethyl is crystallisable and has a sharp taste. Specific gravity 1·043. Melts at 44° and solidifies at 32° C. Sparingly soluble in water, very soluble in alcohol. Chlorine, with the aid of heat, converts it into a crystallisable chlorinated compound. Nitric and sulphuric acids decompose it at the boiling heat, producing benzoic acid. Alcoholic potash converts it into ethylic alcohol and hippurate of potassium.

Hippurate of Methyl. $C^{10}H^{11}NO^3 = C^9H^8(CH^3)NO^3$. (Jacquemin and Schlagdenhauffen, Compt. rend. xlv. 1011.)—Prepared by passing hydrochloric acid gas into a soluton of the acid in wood-spirit heated to 50° or 60° C., washing the resulting syrupy liquid with carbonate of sodium, and then treating it with ether, from which the compound crystallises by spontaneous evaporation.

Hippurate of methyl forms white, transparent needles, soluble in 120 pts. of cold water, and in 60 pts. water at 30°; in boiling water it melts before dissolving. Alcohol and ether dissolve it in all proportions. It melts at 60° and decomposes at 250°, giving off ammonia and benzonitrile. With fuming nitric acid it gives off a combustible gas, probably containing nitrate of methyl. Alkalis decompose it, forming hippuric acid and methylic alcohols. Ammonia converts it into hippuramide.

HIRCIC ACID. The name given by Chevreul (*Recherches sur les corps gras*, pp. 151, 236) to an oily acid, slightly soluble in water, which he obtained from mutton-suet, and to which he attributes the peculiar taste and odour of that substance. The *potassium-salt* is very deliquescent; the *barium-salt* is sparingly soluble in water and contains 43·8 per cent. barium. The acid is probably nothing more than a mixture of several acids of the series $C^nH^{2n}O^2$.

HISINGERITE. A hydrated silicate of iron occurring at Ridharhyttan in Sweden and other localities. A variety called *Gillingite* is found in the Gillinge mine at Svärta-Kirchspiel in Sweden, and another called Thraulite at Bodenmais in Bavaria. These minerals all contain both protoxide and sesquioxide of iron, and are closely allied in composition; they are, however, but imperfectly crystallised, and have a dark colour, so that impurities in them easily escape detection. Moreover, it is possible that part of the protoxide of iron in the original mineral may be gradually converted into sesquioxide. Hence their constitution cannot be ascertained with certainty. The composition of hisingerite from Ridharhyttan (specific gravity 3·045) agrees however nearly with the formula $3(Fe^2O.SiO^2).2(Fe^4O^3.3SiO^2) + 6H^2O$. Gillingite is the same with 9 at. water; Thraulite is $3(Fe^2O.SiO^2).(Fe^4O^3.3SiO^3) + 6H^2O$. A variety from Orijärfvi in Finland, much richer in protoxide of iron, may be represented by the formula $9(Fe^2O.SiO^3).(Fe^4O^3.3SiO^2) + 9H^2O$. The following are analyses of these minerals:

	SiO^2	Fe^4O^3	Fe^2O	Ca^2O	Mg^2O	H^2O	
a.	33·07	34·78	17·59	2·56	0·46	11·54	= 100·0
b.	32·18	30·10	8·63	5·50	4·22	19·37	= 100·0
c.	31·28	49·12		. .	. .	19·12	= 99·52
d.	29·51	10·74	37·49	. .	7·78	13·00	= 98·52

a, from Ridharhyttan by Rammelsberg (*Mineralchemie*, p. 852).—*b*, from the Gillinge mine by Rammelsberg (*ibid.*).—*c*, Thraulite from Bodenmais by v. Kobell (Pogg. Ann. xiv. 467).—*d*, from Orijärfvi by Hermann. (J. pr. Chem. xlvi. 338.)

HISLOPITE. A grass-green limestone from Takli near Nágpur in Central India, of specific gravity 2·645, and containing 80·79 per cent. carbonate of calcium, 0·73 alumina, a trace of carbonate of magnesium, and 16·63 of an imbedded green silicate (= 98·15), perhaps identical with glauconite. (S. Haughton, Phil. Mag. [4] xvii. 16.)

HITCHCOCKITE. A silicate of lead and aluminium from the Canton mine in Georgia. Specific gravity, 4·024. Contains 20·85 per cent. P^2O^4, 27·40 Pb^2O, 28·41

Al^4O^3, 0·14 PbCl, and 23·20 water (= 100·00), agreeing nearly with the formula, $3Pb^2O.P^2O^5.2[4Al^4O^3.P^2O^5.18H^2O] = Pb^3PO^4.2[(Al^2)'''PO^4.3(Al^2)'''H^3O^3]$. (Genth, Sill. Am. J. [2] xxiii. 424.)

HJELMITE. A mineral consisting chiefly of tantalate of yttrium and iron, found in the neighbourhood of Ytterby, together with garnet, gadolinite, &c. in a rock consisting of quartz, orthoclase, albite, and mica. It has a metallic lustre, granular fracture, pure black colour in the mass, blackish grey in powder. Hardness = 5. Specific gravity = 5·82. It exhibits no distinct indications of crystalline form or cleavage. Its analysis gave:

TaO^3	SnO^2*	Cu^2O	Ca^2O	Y^2O	Ce^2O	U^2O	Fe^2O	Mn^2O	Mg^2O	H^2O	
62·42	6·56	0·10	4·26	5·19	1·07	4·87	8·06	3·32	0·26	3·26	= 99·37

Before the blowpipe it decrepitates and flies to pieces, gives off water, and turns brown without melting, in the oxidising flame; by phosphorus-salt it is easily dissolved to a bluish-green glass; easily also by borax to a clear glass rendered opaque by flaming; by reduction on charcoal with carbonate of sodium, it yields metallic spangles. (Nordenskiold, Pogg. Ann. cxi. 273; Jahresber. 1860, p. 780.)

HOERNESITE. A hydrated arsenate of magnesium from the Bannat, found imbedded in calcspar. It forms rhomboïdal laminæ of 36° and 144°, bevelled on the sides, closely resembling the most common form of gypsum, and probably belonging to the monoclinic system, cleaving perfectly in the direction of the pinacoïdal face, having a mother-of-pearl lustre on the cleavage-faces; white, transparent (translucent in the thicker parts), flexible in thin layers. Hardness = 0·5. Specific gravity = 2·474. Splinters of it melt even in the flame of a candle. An analysis by v. Hauer (Rép. Chim. pure, ii. 286) gave 24·54 per cent. Mg^2O, 46·33 As^2O^5, and 29·07 water (= 99·94), agreeing with the formula, $Mg^3AsO^4.4H^2O$. (Haidinger, Wien. Akad. Ber. xi. 18.)

HOLCUS LANATUS. For the composition of the ash of this grass, see GRASSES (ii. 943).

HOLMESITE. See CLINTONITE (i. 1026).

HOMŒOMORPHISM. See ISOMORPHISM.

HOMICHLIN. A mineral closely related to barnhardtite (i. 508), and copper pyrites (ii. 77), from Plauen in the Saxon Voigtland (and other localities), where it forms, together with carbonate and silicate of copper, a vein of copper-ore imbedded in greenstone. It occurs sometimes in quadratic crystals, but more generally massive. Hardness between 4 and 5. Specific gravity = 4·472 to 4·480. Colour, brass-yellow, but with more of a bronze tint than copper-pyrites, and quickly acquiring a many-coloured tarnish. Streak black. According to an analysis by Richter, it contains 25·81 per cent. iron, 43·76 copper, and 30·21 sulphur, agreeing with the formula, $3Ccu^2S.Fe^4S^3.2Fe^2S$, or $(Ccu^3Fe^2fe^3)S^4$. (Breithaupt, Sill. Am. J. [2] xxviii. 132; xxix. 373. *Rammelsberg's Mineralchemie*, pp. 426, 987.)

HOMOCUMINIC ACID. $C^{11}H^{14}O^2 = \left.\begin{matrix}C^{11}H^{13}O\\H\end{matrix}\right\}O$. *Cyminic acid.* (Rossi, Compt. rend. lii. 403; Ann. Ch. Pharm. Suppl. i. 139.)—An acid homologous with cuminic acid, prepared by treating cyanide of cymyl, $C^{10}H^{13}Cy$ (obtained by the action of cyanide of potassium on the chloride, ii. 296), with potash-ley at the boiling heat:

$$C^{10}H^{13}.CN + 2H^2O = C^{11}H^{14}O^2 + NH^3.$$

It crystallises in small needles; melts at 52°; distils without decomposition; dissolves sparingly in cold, easily in boiling water, also in alcohol and ether, reddens litmus and decomposes carbonates. The *potassium-salt* is deliquescent; the *barium-* and *calcium-salts* crystallise in needles; the *magnesium-salt* in nacreous scales; the *silver-salt* has the composition $C^{11}H^{13}AgO^2$.

The low melting point of this acid raises a doubt as to whether it is the true homologue of cuminic acid (which melts at 92°) or an isomer of that homologue related to it in the same manner as the acid $C^8H^8O^2$, obtained by Cannizzaro from cyanide of benzyl (probably α-toluylic acid), is related to the true toluylic acid.

HOMOLACTIC ACID. This name was given by Cloez (Compt. rend. xxxiv. 364) to an acid, isomeric if not identical, with glycollic acid, found in the mother-liquor which is obtained in the preparation of fulminating mercury. By neutralising this liquor with chalk, distilling off the volatile products (acetic ether, &c.), repeatedly crystallising the remaining solution by spontaneous evaporation, and decanting the liquid containing the more soluble salts, the calcium-salt of this acid was obtained in small light nodules resembling lactate of calcium.—The acid itself formed, when concentrated, a syrup which did not crystallise. The silver-salt crystallised in long thin laminæ, sparingly soluble in cold water.

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* With tungstic anhydride.

HOMOLOGOUS SUBSTANCES. This term is applied to organic compounds differing from one another in composition by CH^2 or any multiple thereof; for example, the *alcohols* $C^nH^{2n+2}O$, the *fatty acids* $C^nH^{2n}O^2$, and the *aromatic acids* $C^nH^{2(n-4)}O^2$.—Bodies thus related exhibit, for the most part, a regular gradation of properties, both physical and chemical. Thus, in the series of fatty acids, formic acid, CH^2O^2, and acetic acid, $C^2H^4O^2$, are watery liquids without any trace of viscosity; propionic acid, $C^3H^6O^2$, is slightly oily; butyric acid, $C^4H^8O^2$, valeric acid, $C^5H^{10}O^2$, and a considerable number of others exhibit more and more of an oily or fatty character as their atomic weights increase; while palmitic acid, $C^{16}H^{32}O^2$, and stearic acid, $C^{18}H^{36}O^2$, and a few others, are at ordinary temperatures solid fats, exhibiting higher melting points as they rise higher in the series; and lastly cerotic acid, $C^{27}H^{54}O^2$, and melissic acid, $C^{30}H^{60}O^2$, are of the consistence of wax. Similar relations are observed in the series of alcohols, corresponding with these acids. Moreover, the chemical energy of bodies thus related continually decreases as their molecules become heavier. Common alcohol is violently decomposed by potassium and sodium, with rapid evolution of hydrogen; but on the fatty alcohols, these metals act but very slowly. Similar differences of character are observed between the higher and lower terms of the fatty acid series. Formic and acetic acids are highly corrosive liquids, which unite energetically with bases, and decompose carbonates with the greatest ease; whereas the solid fatty acids, stearic, palmitic acid, &c., exert no action on the animal tissues, do not enter readily into direct combination with any bases excepting the strongest, and decompose carbonates but slowly.

Bodies belonging to the same homologous series exhibit, for the most part, regular gradations of boiling point and of atomic volume. With regard to the latter, Kopp has shown that compounds whose chemical formulæ differ by $n\,CH^2$, differ in atomic volume by $n.22$ (i. 444). The relations of boiling point exhibited by homologous liquids are fully detailed in the article Heat (p. 89).

Various attempts have been made of late years to build up the terms of homologous series, the higher from the lower. Frankland and Kolbe in 1847 (Ann. Ch. Pharm. lxv. 288) showed that a cyanide of an alcohol-radicle of the series C^nH^{2n+1}, may be converted into the next higher acid by boiling with aqueous potash, the action consisting in the assumption of the elements of water, with elimination of ammonia, *e.g.*:

$$\underset{\text{Cyanide of methyl.}}{CH^3.CN} + 2H^2O = \underset{\text{Acetic acid.}}{C^2H^4O^2} + NH^3;$$

and generally

$$C^nH^{2n+1}.CN + 2H^2O = C^{n+1}H^{2n+2}O^2 + NH^3.$$

Another method of passing from an alcohol to the next higher acid was discovered in 1859 by Wanklyn (Proc. Roy. Soc. x. 21), who showed that sodium-ethyl (prepared from zinc-ethyl, which is itself obtained from iodide of ethyl, and this from ethylic alcohol) exposed to the action of carbonic anhydride, absorbs that gas, and is converted into propionate of sodium:

$$C^2H^5Na + CO^2 = C^3H^5NaO^2.$$

Neither of these reactions, however, affords the means of obtaining one alcohol of the series from the next below it, because no method has yet been discovered of converting a fatty acid into the corresponding alcohol.

The great problem of passing from one alcohol to that next above it has, however, been solved in a general way by Mendius (Ann. Ch. Pharm. cxxi. 129), whose method consists in exposing the cyanides of the alcohol-radicles to the action of nascent hydrogen, thereby converting them into the amines of alcohol-radicles higher than the radicles started from. In this manner, starting from hydrocyanic acid, he obtains methylamine, thus:

$$\underset{\text{Cyanide of hydrogen.}}{HCN} + H^4 = \underset{\text{Methylamine.}}{CH^5N}$$

Methylamine treated with nitrous acid yields methylic alcohol (see Amines, i. 174); this compound may be converted by well-known processes into cyanide of methyl; and this cyanide treated with nascent hydrogen yields ethylamine:

$$\underset{\text{Cyanide of methyl.}}{CH^3.CN} + H^4 = \underset{\text{Ethylamine.}}{C^2H^7N}.$$

From this last compound, by similar processes, we may ascend to the tritylic or propylic stage, and thus, by a repetition of the same reactions, the series of alcohols

$C^nH^{2n+2}O$ may be ascended, step by step. The general equation representing the passage from an alcoholic cyanide of this series to the next highest amine is:

$$C^nH^{2n+1}.CN + H^4 = C^{n+1}H^{2n+5}N.$$

This reaction will in all probability be found to succeed with cyanides derived from alcohols of the aromatic and other series, and thus a general method of producing an alcohol of any series from the one next below it may be obtained.

Carius (Ann. Ch. Pharm. cxxvi. 215), by heating ethyl-gas (C^4H^{10}) to 100° with bromine, has obtained a liquid having the composition and boiling point of dibromide of tetrylene:

$$C^4H^{10} + Br^4 = C^4H^8Br^2 + 2HBr.$$

This compound, if really identical with dibromide of tetrylene, might be converted by known processes into hydrate of tetrylene; and this by the action of hydriodic acid into iodide of tetryl; whence, by distillation with potash, tetrylic alcohol might be obtained. This process appears then to give the means of mounting up the series by two steps at once. Lastly, **Schorlemmer**, by subjecting ethyl-amyl, $C^2H^5.C^5H^{11}$ (isomeric with hydride of heptyl, $C^7H^{15}.H$), to the action of chloride of iodine, has obtained a chloride, $C^7H^{15}.Cl$, which appears to be identical with chloride of heptyl obtained from the hydride of that radicle (p. 144). The problem of ascending from one alcohol to another in an homologous series appears therefore to be capable of solution in several different ways.

For speculations on the cause of homology, and the relations between homologous compounds of different series, see **Carius** (Ann. Ch. Pharm. cxxvi. 210).

HONEY. The honey of the common bee contains cane-sugar, inverted sugar (ii. 864), and an excess of dextroglucose. The proportion of cane-sugar varies with the age of the honey, as it is gradually converted into inverted sugar by the action of a ferment contained in the honey. According to **Soubeiran** (Compt. rend. xxviii. 774), bees' honey contains, besides dextroglucose and a dextro-rotatory sugar capable of inversion (? cane-sugar), likewise an uncrystallisable sugar, possessing a lævo-rotatory power three times as great as that of inverted sugar. The honey of the *Polybia apicipennis*, a kind of wasp widely distributed in tropical America, yields cane-sugar in large crystals (**H. Karsten**, Pogg. Ann. c. 550). The honey of the Mexican honey-ant is, according to **C. M. Wetherill** (Chem. Gaz. 1853, 72), a nearly pure solution of uncrystallisable sugar, $C^6H^{14}O^7$ (dried in vacuo); it has a slight acid reaction, and the volatile acid contained in it reduces oxide of silver like formic acid.

HONEY-STONE. See MELLITE.

HOP. (*Humulus Lupulus.*)—The fruit of the hop is formed of small membranous cones, at the base of which is found a yellow bitter powder called **lupulin** (*q. v.*), containing, according to an analysis by Yves[*], 36 per cent. resin, 12 wax, 11 of a peculiar bitter principle soluble in water and alcohol, 5 tannin, 10 extractive matter insoluble in alcohol, and 26 of residue insoluble in water. Yves found in hop-cones dried at 30° C., 10 per cent. of lupulin. According to Payen and Chevallier, the proportion of crude lupulin is 13 per cent., about 4 per cent. of which consists of minute particles of the cones themselves, resulting from the sifting.

Lupulin distilled with water yields valerianic acid and a volatile oil, containing a hydrocarbon, $C^{10}H^{16}$, together with valerol, $C^6H^{10}O$ (see HOPS, OIL OF). The resinous matter which remains after the distillation still retains a considerable portion of valerol, and, when distilled with slaked lime, yields valeraldehyde, $C^5H^{10}O$.

Lupulin treated with alcohol yields, according to Payen, Chevallier, and Pelletan, about 65 per cent. of its weight. The dissolved portion consists almost wholly of resin, extractive matter, and tannin, the two latter soluble in water, whereas the resin, which forms about 52 per cent. of the lupulin, is insoluble. This resin, when purified by repeated solution in alcohol, precipitation by water, and drying, gives by analysis numbers which may be represented by the formula, $C^{54}H^{70}O^{11}$, together with a quantity of water varying between 1 and 6 H^2O, according as the resin has been more frequently dissolved in alcohol and reprecipitated by water.

The bitter principle isolated by Payen, Chevallier, and Pelletan, and called by them **lupulite** (or true **lupulin**), amounts to between 8·3 and 12·5 per cent. of the lupulin. It remains dissolved, together with malic acid, in the water in which lupulin has been digested. To isolate it, the free acid is saturated with chalk, the liquid evaporated to dryness, and the residue treated with ether, which dissolves a small quantity of resin. The lupulite is then separated from the malate of calcium by solution in alcohol, and evaporated to dryness. Lupulite thus prepared is white or yellowish, or sometimes reddish yellow, sometimes translucent, sometimes opaque. It has no odour, unless when strongly heated, in which case it exhales the odour of hops (perhaps in consequence of retaining a small portion of essential oil); it possesses the characteristic taste of hops. It has not been analysed. It is soluble in alcohol, but nearly insoluble in ether. By dry distillation it yields a considerable quantity of empyreumatic oil, but no ammoniacal products.

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[*] *Composition du houblon*, par MM. Yves, Payen, Chevallier, Pelletan, Wagner, Vlaanderen: *Résumé présentant l'état de la question*, par E. Kopp. (Rép. Chim. app. 1860, p. 21.)

The tannin or astringent principle of the hop was for a long time regarded as identical with gallotannic acid, and as capable of conversion into gallic acid, and this change was supposed to account for the fact that old hops are not capable of clarifying beer. But, according to A. Wagner, gallic acid cannot be detected, even in very old hops quite unfit for making beer. He regards the tannic acid of hops as identical with morintannic acid, and finds that it amounts to between 3·2 and 5·7 per cent. of the hops.

According to Payen and Chevallier, the active principles of the hop do not reside exclusively in the lupulin, as was formerly supposed; they found, indeed, that hop-cones completely freed from lupulin, still yielded about 26 per cent. of substances soluble in alcohol.

To discover whether hops have been sulphured, Wagner treats them with granulated zinc, water, and pure hydrochloric acid. Any sulphurous acid that may be present is then reduced by the nascent hydrogen, and the liberated sulphur uniting with the hydrogen, forms sulphydric acid, which, if passed into a solution of nitroprussiate of sodium, generates a deep purple colour (ii. 257). This reaction will detect extremely small quantities of sulphurous acid; larger quantities may be detected by the odour, by the precipitation of iodine from a solution of iodate of potassium, and by various other reactions.

The ashes of hop-cones yield by analysis the following results:—

	Way and Ogston.*			H. Watts.†
	Bentley variety.	Golding variety.	Grape variety.	Grape variety.
Potash	11·98	24·88	25·56	19·41
Soda	. .	. .	. .	0·70
Lime	17·93	21·59	18·47	14·15
Magnesia	5·94	4·69	5·27	5·34
Alumina	. .	. .	. .	1·18
Ferric oxide	1·86	1·75	1·41	2·71
Sulphuric acid (SO^3)	7·01	7·27	11·68	8·28
Chlorine	. .	. .	. .	2·26
Silica	22·97	19·71	9·99	17·88
Carbonic acid (CO^2)	5·44	2·17	4·54	11·01
Phosphoric acid (P^2O^5)	21·38	14·47	17·58	14·64
Chloride of potassium	5·45	. .	4·34	
Chloride of sodium	. .	3·42	0·12	
Charcoal and loss	. .	. .	. .	2·44
	99·96	99·95	98·96	100·00
Ash per cent. of the dry substance	8·07	5·95	7·21	
„ „ „ fresh „	7·27	5·22	6·52	6·5

The hops analysed by Watts were grown on a heavy clay-soil near Hawkhurst in Kent. The crop was rather above the average, viz. 12 cwt. to the acre. By comparing this amount with the analysis of the ash, it is found that the hops grown on an acre of ground extracted from the soil 87 pounds of mineral constituents, including 12 to 13 oz. of phosphoric acid (P^2O^5), 17 lbs. potash (K^2O), and 15 lbs. 10 oz. of silica. This is sufficient to account for the well-known exhaustive effect of this plant on the soil. (For the statistics of the growth of hops in this country, see *Ure's Dictionary of Arts*, &c., ii. 460.)

HOPEITE. A cadmiferous zinc-ore from the calamine mines of Altenberg, near Aix-la-Chapelle. It has not been completely analysed, but appears to be a hydrated phosphate of zinc, containing a small quantity of cadmium. It forms transparent or translucent prisms, belonging to the trimetric system, having a greyish-white colour and vitreous lustre. It occurs also in reniform masses and amorphous. Specific gravity 2·76 to 2·85. Hardness 2·5 to 3. It is sectile. (Dana, ii. 419.)

HOPS, OIL OF. Hop-cones or lupulin distilled with water, yield an essential oil having the odour of thyme, and consisting, according to R. Wagner (Dingl. pol. J. cxxviii. 217), of a hydrocarbon isomeric with oil of turpentine, and an oxygenated oil, apparently identical with valerol, $C^6H^{10}O$, and convertible by oxidation into valerianic acid, and perhaps also some of its higher homologues: hence the odour of old cheese, which hops acquire by keeping. The non-oxygenated oil is not altered by contact with the air, but the greater part of it is gradually dissipated by volatilisation.

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* Journal of the Royal Agricultural Society, pt. i. (1849); Jahresber. 1849, p. 679.
† Phil. Mag. [3] xxxii. 54; Jahresber. 1847-8, p. 1077.

According to Personne (J. Pharm. [3] xxvi. 2419; xxvii. 22), lupulin distilled with water, yields valerianic acid and an essential oil lighter than water, colourless and neutral after rectification, but becoming acid and resinous after some time. It begins to boil at 140° C., but the boiling point gradually rises to 300°. The portions distilling between 150° and 160°, and those which distil at about 300°, appear to have the same composition, viz. $C^{11}H^{18}O$. Both these portions of the distillate turn the plane of polarisation to the right; remain fluid at − 17°; dissolve without red colour in sulphuric acid; are converted by nitric acid into valerianic acid and a resinous substance; and when let fall by drops on melting caustic potash, yield a hydrocarbon, $C^{10}H^{16}$, and valerate of potassium. Hence, Personne regards the volatile oil of lupulin as analogous to essence of valerian, which, according to Gerhardt, consists of borneene, $C^{10}H^{16}$ (i. 626), and valerol, $C^6H^{10}O$. The hydrocarbon from oil of hops is not, however, identical with borneene, inasmuch as it cannot be converted into borneol.

HORDEIN. Barley-starch obtained by kneading barley-meal in water, and leaving the liquid to settle, does not dissolve completely when warmed with acidulated water, but leaves a pulverulent substance, to which Proust gave the name *hordein*. It appears, however, to be, not a definite substance, but a mixture of starch, cellular tissue, and an azotised body.

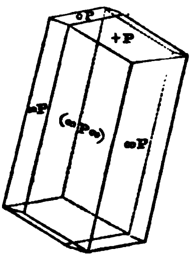
HORDEUM VULGARE. *Barley.*—The composition of the grain of barley, as determined by various observers, has been already given in the article CEREALS (i. 825); also the composition of the ash of the grain, and of the straw and chaff, as determined by Way and Ogston, showing the limits between which the amounts of each constituent was found to vary. The following table (p. 168) contains a more detailed statement of the results of these ash-analyses.

HORN. See HORNY TISSUE (p. 170).

HORNBLENDE. *Amphibole.*—A mineral which plays an important part in the composition of rocks of the primitive and transition periods. Hornblende-rock and hornblende-slate consist almost entirely of it, and, in diorite (greenstone), syenite, hornblende-gneiss, &c., it enters as an essential constituent.

Hornblende forms prismatic crystals belonging to the monoclinic system. Ratio of axes, $a : b : c$, = 1·837 : 1 : 0·5401. Inclination of the clinodiagonal (b) to the principal axis (c) = 75·10°. The angle $\infty P : \infty P$ = 55° 30′; $+P : +P$ in the clinodiagonal principal section = 148° 30′; $oP : \infty P$ = 76° 59′. Ordinary combination $\infty P . [\infty P\infty] . +P . oP$. (*Fig. 556a.*) Twins with face of composition parallel to $\infty P\infty$, as in the figure. Cleavage perfect, parallel to ∞P. It is also found imperfectly crystallised; fibrous or columnar, coarse or fine, with fibres often like flax; sometimes lamellar, also granular, coarse or fine, and usually strongly coherent; sometimes friable. Hardness 5 to 6. Specific gravity 2·9 to 3·4. Lustre vitreous to pearly on cleavage-faces; fibrous varieties often silky. Colour varying from black to white, through various shades of green, inclining to blackish-green; common hornblende, which contains much iron, is nearly black. Streak uncoloured or paler than the mineral. Sometimes nearly transparent, usually translucent to opaque. Fracture subconchoïdal, uneven.

Fig. 556a.



The chemical composition of hornblende was formerly represented, in accordance with the results of older analyses, by the general formula $5M^2O.6SiO^2$ (or $4MO.3SiO^3$); but Rammelsberg (*Mineralchemie*, pp. 426, 494,) has shown, by comparison of the more recent analyses by himself and others, that all hornblendes are metasilicates, of the general formula $M^2O.SiO^2$ or M^2SiO^3. The metals included under the general symbol M are calcium, magnesium, iron and sodium, sometimes also manganese and potassium. These metals, replacing one another isomorphously, give rise to a great number of substances differing considerably in composition as well as in colour and other physical properties. A further variation is caused by the presence in many varieties of alumina, which enters, not in place of the protoxides M^2O, for the amount of the latter is not found to be in inverse proportion to that of the alumina, but in place of a certain portion of the silica, and in such proportion, according to Bonsdorff, that 1 at. SiO^2 may be regarded as isomorphously replaced by 1 at. AlO^3 ($2SiO^3$ by $3Al^2O^3$), but according

Composition of the Ash *of the* Grain *and* Straw *of* Barley

	Grain.									Straw (with chaff).				
	Chevalier barley					Barley from Moldavia			Long-eared Nottingham on sandy soil.	Moldavia barley raised on clay soil.	Chevalier barley.			Long-eared Nottingham raised on calcareous soil.
		raised on clay-soil.	raised on sandy soil.	raised on loamy soil.	raised on calcareous soil.		raised on clay soil.	raised on sandy soil.			raised on clay soil.	raised on loam soil.	raised on calcareous soil.	
Potash	26·83	22·43	24·97	28·60	37·22	19·78	26·61	22·46	32·02	12·69	11·22	14·37	20·18	16·18
Soda	. .	1·42	0·51	. .	. .	0·89	1·26	4·93	1·21	2·65	. .	0·28	3·29	. .
Lime	3·62	1·96	2·97	2·97	2·92	4·20	1·26	1·88	3·39	5·34	5·79	8·50	11·90	12·59
Magnesia	4·78	10·00	8·00	6·90	7·63	8·15	9·32	8·47	10·99	2·65	2·70	1·70	2·93	2·99
Ferric oxide	1·54	0·87	0·84	1·46	trace	0·93	0·24	0·10	0·15	0·10	1·72	0·20	0·31	0·32
Sulphuric acid (SO^3)	1·30	2·82	0·92	trace	0·26	0·39	0·47	0·53	trace	0·53	2·71	2·22	3·18	3·04
Silica	29·79	22·25	22·08	18·47	17·27	27·66	30·35	28·09	21·12	63·29	68·50	62·79	48·18	52·40
Carbonic anhydride (CO^2)	4·35	. .	. .	. .	. .	. .	. .	. .	0·48	. .	. .	1·25	3·55	3·89
Phosphoric anhydride (P^2O^5)	25·32	37·67	38·26	38·78	30·76	37·99	30·08	32·92	29·92	3·24	7·20	4·22	3·41	2·13
Chloride of potassium	. .	. .	. .	1·29	1·93	. .	. .	. .	. .	. .	. .	. .	. .	0·90
Chloride of sodium	2·47	0·56	1·44	1·59	2·01	trace	0·41	0·61	0·72	5·68	2·14	4·37	3·07	5·46
	100·00	99·98	99·99	100·00	100·00	99·99	100·00	99·99	100·00	99·97	100·00	100·00	100·00	100·00
Ash in 100 pts. of dried substance	2·32	2·65	2·47	2·28	2·39	2·28	2·55	2·07	2·20	6·80	. .	5·49	3·65	1·51
Ash in 100 pts. of fresh substance	2·03	2·30	2·15	2·07	2·13	2·03	2·31	1·79	1·99	6·12	. .	4·97	3·34	1·37
Moisture in 100 pts. of air-dried substance	12·50	18·20	13·20	9·20	11·16	11·24	13·00	10·00	9·20	10·00	. .	9·50	8·58	9·25
Sulphur in 1000 pts. of dry substance	3·53	0·96	1·21	0·74	1·83	2·42	1·54	1·58	1·41	1·56	. .	1·02	0·54	2·05

The results of these analyses show that, in barley as in other cereals, the amount of ash is but little influenced by the nature of the soil, but is for the most part greatest in plants grown on clay soils. The amount of ash in the straw and chaff varies between wider limits than that of the grain; the latter varies as much in plants growing on the same as in those growing on different soils. The composition of the ash of barley-grain does not differ essentially from that of wheat (*q. v.*) in any respect excepting in containing a larger amount of silica.

to Rammelsberg, in the proportion of $2Al^4O^3$ for $3SiO^2$ or Al^8 for Si^3, the quantity of oxygen in the acid constituent of the mineral remaining unaltered.

Many varieties of hornblende likewise contain small quantities of fluorine, probably, according to Rammelsberg, in the form of a double fluoride of silicon and calcium, or magnesium. Titanium is also sometimes present in small quantity.

The pale varieties of hornblende containing no iron fuse readily before the blowpipe, with intumescence, forming a glass which is either transparent or exhibits various degrees of translucence down to milk-white opacity. With borax they form a colourless glass. The lighter coloured ferruginous varieties fuse alone, with more or less difficulty, to a dark yellowish glass, and give with borax a transparent glass tinged with iron. The darker green varieties afford a deeper iron colour. Hornblende containing alumina and a little iron, acts much like the non-ferruginous varieties; but the black varieties fuse to a brilliant black bead and give with borax a glass tinged with iron. *Anthophyllite* melts with difficulty to a glass coloured by iron.

The following are analyses and descriptions of the principal varieties of hornblende.

I. *Hornblendes with little or no Alumina.*

	SiO^2	Mg^2O	Ca^2O	Fe^2O	Mn^2O	Al^4O^3	Loss by ignition.		
Tremolite:									
1. St. Gothard, *white* . .	57·72	27·45	13·95	. .	. .	. .	0·33		= 99·45
2. Gouverneur, N. Y. . .	57·40	25·69	13·89	1·36	. .	0·38	0·40		= 99·12
3. Greenland, *greenish white* .	54·71	23·92	15·06	2·41	. .	. .	3·33		= 99·43
4. Tyrol, *Asbestos* . . .	57·50	23·09	13·42	3·88	. .	. .	2·36		=100·25
Actinolite:									
5. Arendal, *grey-green* . .	56·77	21·48	13·56	5·88	. .	0·97	2·20		=100·86
6. Helsingfors, „ . .	57·20	9·45	21·20	11·75	1·15	0·20	. .		=100·95
Anthophyllite:									
7. Kongsberg, Norway . .	56·74	24·35	. .	13·94	2·38	. .	1·67		= 99·08
8. Kupferberg, Bavaria . .	55·59	30·46	1·76	8·40	. .	4·03	. .		=100·24
9. Perth, Upper Canada .	57·60	29·30	3·55	2·10	. .	3·20	3·55		= 99 30
10. Cummington, Mass. .	50·91	10·30	. .	32·60	. .	0·92	3·04	Na^2O 0·65	= 98·42
11. Ural, *Asbestos* . . .	58·72	30·90	. .	8·10	. .	0·19	1·58		= 99·49
Cummingtonite:									
12. Cummington, Mass. . .	48·91	2·35	2·00	. .	46·74	. .	. .		=100·00
13. „ „ . .	51·21	. .	2·93	4·34	42·65	. .	. .		=101·13

1. 2. 3 Rammelsberg (Pogg. Ann. ciii. 273, 435; *Mineralchemie*, p. 468).—4. Scherer (Pogg. Ann. lxxxiv 231).—5. Rammelsberg (*loc. cit.*)—6 Popping (Berz. Jahresber. xxvii. 252).—7. Vopelius (Pogg. Ann. xxii. 358).—8. Sackur (Rammelsberg's *Mineralchemie*, *loc. cit*).—9. Thomson (Rec. Gen. Sci. xvii.).—10. Smith and Brush (Sill. Am. J. [2] xvi. 218).—11. Heintz (Pogg. Ann. lviii. 168).—12. Hermann (J. pr. Chem. xlvii. 7).—13. Schlieper (Sill. Am. J. [2] ix. 410).

a. Tremolite or *Grammatite*, $\left.\begin{matrix}Ca\\Mg^3\end{matrix}\right\}Si^2O^6 = Ca^2SiO^3.3Mg^2SiO^3$, is white, or with a greyish, greenish, or yellowish tinge. Crystals often in long slender blades, either distinct and traversing the gangue, or aggregated in columnar and radiated masses. Specific gravity 2·93. Transparent or translucent. Found in the Tremola valley, Switzerland, and on the St. Gothard, in granular limestone or dolomite; in the Tyrol, the Bannat, at Gülsjo in Sweden, &c. *Calamite* is an asparagus-green variety o tremolite, found in prisms in serpentine, at Normarken in Sweden.

b. Actinolite (*Actinote*, *Strahlstein*).—This name includes hornblendes which are isomorphous mixtures of metasilicates containing chiefly magnesium, calcium, and iron, their general formula being $(Mg; Ca; Fe)^2SiO^3$. Actinolite occurs in bright green, bladed crystals, or columnar forms; if in distinct rays, it is called *glassy actinolite*. The crystals are long slender prisms, breaking easily in the transverse direction. Specific gravity usually between 3·02 and 3·05. Actinolite occurs at Greiner in the Zillerthal; at Arendal in Norway; at Helsingfors, and several other places in Finland; at Taberg in Sweden, and in Pennsylvania. *Raphilite* is an asbestiform actinolite from Lanark in Canada.

Asbestos (i. 415), when of a white colour or some light shade, is usually a fibrous variety of tremolite or actinolite. The darker specimens are varieties of anthophyllite.

c. Anthophyllite.—This variety occurs in masses of a fine columnar structure, or made up of acicular fibres of brown or greyish brown colour, often with submetallic lustre. Specific gravity 2·9 to 3·16. The cleavage affords prisms of 124° 30′, like other varieties of hornblende. Anthophyllites are found at Kongsberg in Norway, Kupferberg in Bavaria, Perth in Upper Canada, and Cummington in Massachusetts.

The hornblendes included under this name vary considerably in composition; that from Kongsberg consists of $\left.\begin{matrix}Fe\\Mg^3\end{matrix}\right\}Si^2O^6$, or $Fe^2SiO^3.3Mg^2SiO^3$; that from Kupferberg contains twice as much magnesia, its formula being $Fe^2SiO^3.6Mg^2SiO^3$. The minerals from Canada and Massachusetts are altered anthophyllites, the latter being approximately represented by the formula, $Mg^2SiO^3.3Fe^2SiO^3$.

d. Cummingtonite is a rose-red granular hornblende from Cummington, Massachusetts, of specific gravity 3·42, and consisting of manganous silicate, Mn^2SiO^3.

e. Arfvedsonite.—This is a black mineral found in Greenland, accompanying eudialyte. It was formerly regarded as a variety of hornblende, with which indeed it is isomorphous; but, according to Rammelsberg, it is a distinct species, whose formula is $(2M^2O.SiO^2)\ Fe^4O^3.3SiO^2$, or $\left.\begin{matrix}M^4\\ fe^6\end{matrix}\right\}Si^4O^{13}$. Rammelsberg's analysis gives 51·22 per cent. SiO^2, 23·75 Fe^4O^3, 7·80 Fe^2O, 1·12 Mn^2O, 2·08 Ca^2O, 0·90 Mg^2O, 10·58 Na^2O, 0·68 K^2O, 0·16 water, and a trace of alumina.

II. *Hornblendes containing Alumina.*

	SiO^2	TiO^2	Al^4O^3	Fe^4O^3	Fe^2O	Mn^2O	Mg^2O	Ca^2O	Na^2O	K^2O	F	H^2O
1. Orange Co., N. Y., *limpid crystals*	51·67	. .	5·75	2·86	. . .	. .	23·37	12·42	0·75	0·81	. .	0·46=98·12
2. Brevig, Norway, *black* . .	42·27	1·01	6·31	6·62	21·72	1·13	3·62	9·68	3·14	2·65	. .	0·48=98·63
3. Vesuvius . .	39·92	. .	14·10	6·00	11·03	0·30	10·72	12·62	0·55	3·37	. .	0·37=98·98
4. Pargas, Finland, *light green* . .	46·12	. .	7·56	. .	2·27	. .	21·23	13·70	2·48	1·29	2·76	1·10=98·50
5. Ural, *greenish black*	44·24	1·01	8·85	5·13	11·80	. .	13·46	10·82	2·08	0·24	0·25	0·39=98·27
6. Val de Bove, Etna	40·91	. .	13·68	. .	17·48	. .	13·19	13·44	. .	. .	. .	0·85=99·55

1—5. Rammelsberg (*Mineralchemie*, p. 490).—6. v. Waltershausen (*Vulkanische Gesteine*).

The minerals included under this head are mixtures of the isomorphous compounds, $M^2O.SiO^2$, $Fe^4O^3.3SiO^2$ and $3M^2O.2Al^4O^3$. (Rammelsberg.)

Common Hornblende.—This name is applied to the dark green and black aluminous varieties, whether in crystals or massive. Specific gravity 3·1 to 3·4. The name alludes to its toughness.—*Carinthin* is an aluminous and ferruginous hornblende from Carinthia. Specific gravity 3·127.

Uralite, from the Ural, has the cleavage structure and composition of hornblende, but the external form of augite, and is regarded as a pseudomorph. The two species are variously mingled in different specimens, showing the change in different stages of progress.

Diastatite is a hornblende from Wermland in Sweden, differing, according to Breithaupt, from common hornblende, by a degree in the angle of the prism. *Pargasite* includes crystallised varieties (crystals usually thick and stout); of high lustre, and rather dark shades of green. It is also granular.

Fine specimens of the dark-coloured hornblendes occur at Aussig and Teplitz in Bohemia; Tunaberg in Sweden, and Pargas in Finland. In Corsica there is found a variety of hornblende (*Verde di Corsica duro*) which admits of a high polish.

Altered forms of Hornblende.—Alterations of hornblende are mostly like those of augite. Varieties often occur, containing water of hydration, especially asbestiform or anthophyllite varieties. The ferruginous change by oxidation is common, and all varieties are exposed to alteration from infiltrating waters, holding carbonates, silicates, &c., in solution, thus giving rise to magnesian, ferruginous, magnesio-ferruginous (chlorite), alkaline, or aluminous forms. Talc, steatite, serpentine, chlorite, mica, pinite, chabasite, limonite, magnetite, occur as hornblende pseudomorphs.

HORNBLENDE-ROCK is a rock consisting either wholly of hornblende or of that mineral mixed with quartz, and occasionally containing mica, iron pyrites, magnetic iron ore, and garnet. *Hornblende-slate* is a slaty variety of hornblende rock. These rocks belong to the oldest formations; they seldom form extended beds, occurring more generally in masses subordinate to granite, gneiss, &c.

HORN-LEAD. *Cerasine.* Native *chlorocarbonate of lead*, $2PbCl.Pb^2CO^3$, so called from its external resemblance to horn.

HORN-QUICKSILVER. Native sub-chloride of mercury. (See MERCURY.)

HORN-SILVER. Native chloride of silver. (See SILVER.)

HORNSTONE. A variety of quartz resembling flint, but more brittle, and with a more splintery fracture. It is often called *Chert*. It is often found as a petrifaction on wood, and is used for making mortars and various other articles.

HORNY TISSUE. *Epidermose.*—The epidermis of animals, hair, wool, silk, feathers, nails, claws, hoofs, horn, scales, &c., are composed, for the most part, of a substance containing less carbon, but more nitrogen and sulphur than the albuminoïds. The epithelium which coats the internal cavities of the animal body, is also similarly constituted.

The substance, called horny tissue or epidermose, which forms the basis of all these structures, is obtained, though very far from pure, by exhausting the parts containing it with boiling alcohol and ether, after they have been comminuted as much as possible. This treatment removes the fatty matters, together with the greater part of the salts and other foreign matters, but it does not ensure the perfect homogeneity of the undissolved residue. It is known, indeed, that the horny tissues are composed of a number of superposed layers, cell-walls and nuclei, which are perhaps not all of the same nature, but yet cannot be separated by the solvents above mentioned.

The substance thus obtained from the various horny tissues, has been analysed by Mulder, Scherer, Frémy and several other chemists, the results of whose analyses, though not agreeing very closely, still show that the substance forming the basis of these several tissues has, in all probability, the same chemical composition.

	(1.) Scherer.[*]								
	Epidermis of Sole of Foot.	Hair of Beard.	Hair of Head.	Horn of Buffalo.	Nails.	Wool.	Quills.	Beard of Feathers.	Lining Membrane of Egg.
Carbon	51·0	50·0	49·9	51·3	50·4	50·0	51·7	51·8	50·0
Hydrogen	6·8	6·7	6·6	6·7	6·8	7·0	7·2	7·1	6·6
Nitrogen	17·2	17·9	17·9	17·2	16·9	17·7	17·9	17·6	16·8
Sulphur	. .	. .	. .	. .	. .	. .	. .	. .	. .
Oxygen	. .	. .	. .	. .	. .	. .	. .	. .	. .

	(2.) v. Laer.	(3.) Schlossberger.	(4.) Mulder.					(5.) Kemp.	(6.) Frémy.		
	Hair.	Horn of Ox.	White hairs of Cow.	Hoofs of Cow.	Hoofs of Horse.	Horn of Cow.	Nails.	Epithelium of Gall-bladder.	Hoofs of Reindeer.	Whalebone.	Scale of Turtle.
Carbon	49·9	51·6	50·5	50·4	50·4	50·0	50·3	51·9	49·5	50·8	53·6
Hydrogen	6·4	6·8	6·8	6·8	7·0	6·8	6·9	8·0	6·2	7·4	7·3
Nitrogen	17·1	16·6	16·8	16·8	16·7	16·5	17·3	14·8	17·4	16·5	16·4
Sulphur	. .	5·0	5·4	3·4	3·0	3·4	3·2	. .	. .	. .	2·0
Oxygen	. .	20·0	20·5	23·4	22·9	23·3	22·3	. .	. .	. .	20·7
		100·0	100·0	100·0	100·0	100·0	100·0				100·0

The proportion of ash is about 1 per cent.

Horny tissue melts when heated, and burns with a bright flame, exhaling a peculiar odour.

When exposed to the action of boiling water in a Papin's digester, it gradually dissolves, yielding an extract, which does not gelatinise on cooling. By simple maceration in water, cold or warm, the horny tissues are gradually loosened, and exhibit a cellular structure more or less distinct.

Caustic potash easily dissolves horny tissue, eliminating ammonia, especially with aid of heat, and forming a yellow solution, which, when treated with acids, gives off sulphydric acid and yields a white precipitate. When fused with *hydrate of potassium* it gives off hydrogen, and forms acetic, butyric, and valerianic acids, also leucine, tyrosine, &c. Strong solutions of caustic potash or soda are the best reagents for bringing out the cellular structure of the different horny tissues, epidermis, nails, horn, &c.

Strong *sulphuric acid* causes horny tissue to swell up, and partly dissolves it when heated. The solution diluted with water becomes turbid when neutralised with an alkali, or mixed with ferrocyanide of potassium. Prolonged ebullition with dilute sulphuric acid yields tyrosine, leucine, ammonia, &c.

Nitric acid, especially if hot, colours horny tissue yellow, and ultimately dissolves it; on addition of ammonia, the yellow solution acquires a darker colour, and finally assumes an orange tint. According to v. Laer, xanthoproteic acid is formed in the first instance, then saccharic, and finally oxalic acid.

Fuming *hydrochloric acid* produces with horny tissue the same blue or violet coloration as with albuminous substances, and gradually dissolves the tissue on boiling. According to v. Laer, hair immersed even in cold concentrated hydrochloric acid dissolves in the course of some weeks.

Acetic acid does not dissolve horny tissue, but only causes it to swell up.

When *chlorine* is passed into water containing in suspension horny tissue (prepared from hair), the tissue undergoes no change in external appearance, but after drying it is harsh to the touch, and dissolves completely in ammonia, with evolution of nitrogen.

HORSE-CHESTNUT. *Aesculus Hippocastanum.*—The bark of this tree contains two fluorescent substances, æsculin (i. 60) and fraxin or paviin (ii. 708). Pelletier and Caventou found in it a greenish fat oil, a red-brown resin, a bitter yellow substance, a peculiar red substance, tannin, and woody fibre.

The fully developed leaves contain quercitrin, which is also found in the ripe seeds, but not in the undeveloped leaves, or in the coatings of the buds, or in the bark of the stem and branches; the leaves which fall in autumn contain only traces of it. (Rochleder, Wien. Akad. Ber. xxxi. 565.)

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[*] (1.) Scherer, Ann. Ch. Pharm. xl. 55.—(2.) v. Laer, *ibid.* xlv. 156, 157.—(3.) Schlossberger (*Gerhardt's Traité*, iv. 197).—(4.) Mulder's *Chemische Untersuch*, No. 2, p. 270.—(5.) Kemp, Ann. Ch. Pharm. xliii. 115.—(6.) Frémy, Ann. Ch. Phys. [3] xlviii. 47.

The seeds contain, according to Tipp (Vierteljahrschr. pr. Pharm. iii. 19), starch (about 14 per cent.), mucilage, gum, a non-drying oil, saponin, a tannic acid which turns iron-salts green, phosphoric acid, and calcium-salts. Frémy found in the seeds, saponin, a yellow colouring matter [? quercitrin] and a crystallisable bitter substance. Attempts have been made at various times to render the starch of horse-chestnut seeds fit for food by freeing it from the bitter substance by means of a weak alkaline ley. According to Flandin (Compt. rend. xxvii. 391) this is best effected by kneading the peeled and bruised seeds with water containing from $\frac{1}{100}$ to $\frac{1}{50}$ of their weight of carbonate of soda, and then washing them; perfectly white starch then separates, which may be used as an addition to wheat-flour. According to Belloc, the same result may be obtained by the use of pure water. But according to Flandin, the alkali is required to remove an acrid substance and an acid resin, as well as the bitter principle. (Compt. rend. xxviii. 83, 138.)

The cotyledons of horse-chestnut seeds have lately been examined by Rochleder (Wien. Akad. Ber. xlv.; Rép. Chim. pure, 1863, p. 219), who finds, in the alcoholic extract, a bitter substance, argyrescin, an amorphous yellow colouring matter, and a substance which he calls aphrodescin, formerly regarded by Frémy as saponin. These substances are extracted by successive treatment with alcohol, acetate of lead, water, and ether.

Argyrescin, $C^{54}H^{86}O^{24}$, is soluble in water and in alcohol, and is precipitated by ether from its solution in absolute alcohol. When the aqueous solution is evaporated, it remains in the form of a gummy mass. From its solution in weak alcohol, it separates on evaporation in microscopic crystals, having a silvery lustre. The crystals have the composition $2C^{54}H^{86}O^{24}.H^2O$. It dissolves in strong sulphuric acid, forming a solution which turns red when mixed with water. It is fusible, and burns with a very smoky flame.

Argyrescin is resolved by *acids* into argyrescetin and glucose:

$$C^{54}H^{86}O^{24} = C^{42}H^{62}O^{12} + 2C^6H^{12}O^6;$$

and by *alkalis* into æscinic acid, $C^{48}H^{80}O^{23}$, and propionic acid:

$$C^{54}H^{86}O^{24} + 3H^2O = C^{48}H^{80}O^{23} + 2C^3H^6O^2.$$

With alkalis, however, an intermediate product is sometimes obtained, namely, an acid whose barium-salt has the composition $C^{51}H^{82}Ba^2O^{24}$, thus:

$$C^{54}H^{86}O^{24} + 2H^2O = C^{51}H^{84}O^{24} + C^3H^6O^2.$$

This new acid likewise exists, ready-formed, in the cotyledons.

Aphrodescin, $C^{52}H^{84}O^{23}$, is soluble in water, and is precipitated from the hot solution by hydrochloric acid in bulky flocks. It is distinguished from saponin by its solubility in alcohol, and by its reaction with alkalis, which is similar to that of argyrescin, excepting that it yields butyric instead of propionic acid; thus:

$$C^{52}H^{84}O^{23} + 2H^2O = C^{48}H^{80}O^{23} + C^4H^8O^2.$$

Aescinic acid, $C^{48}H^{80}O^{23}$, is obtained by precipitation from its salts, as a gelatinous mass, becoming pulverulent when dry. When boiled with a quantity of alcohol not sufficient to dissolve it completely, it becomes partly crystalline, but does not alter in composition. By drying at 130° in a current of carbonic anhydride, it undergoes a decomposition, which Rochleder represents by the improbable equation $C^{192}H^{151}O^{89} = C^{96}H^{80}O^{46}$ (æscinic acid) + $C^{96}H^{71}O^{43}$.

Aescinate of potassium, $C^{48}H^{79}KO^{23}$, is crystallisable.—The *barium*-salt has the composition $C^{48}H^{78}Ba^2O^{23}$.—The *lead*-salt contains a still larger proportion of base.

Argyrescin, aphrodescin, and æscinic acid heated with hydrochloric acid, are resolved into sugar and a new substance, telescin $C^{36}H^{62}O^{14}$, or a product containing $C^{42}H^{70}O^{18}$. When these decompositions take place in alcoholic solutions, the products formed are not constant, because the telescin may then be further resolved into mannitan (?) and a compound isomeric with quinovic acid.

Aescinic acid, or rather telescin, dissolved in alcohol, mixed with hydrochloric acid, and boiled till a red colour is produced, undergoes a final decomposition, yielding a solution from which water throws down flocks of aescigenin, $C^{24}H^{40}O^4$, isomeric with choloïdic and with quinovic acid. This substance is soluble in sulphuric acid, and on adding sugar to the solution, a red colour is produced similar to that exhibited by the biliary acids when similarly treated.

The action of hydrochloric acid on an alcoholic solution of telescin or æscinic acid sometimes also yields an intermediate product $C^{30}H^{50}O^6$, which is isomeric with

Ash of Horse-chestnut (Wolff).

	Young bark.	Young wood.	Leaf-stalks.	Young leaves.	Flower-stalks.	Calyx and Ovary.	Stamens.	Petals.	Young fruit.	Kernel of ripe fruit.	Green husk of fruit.	Kernel of fruit.	Green husk of fruit.	Brown husk of ripe fruit.
										On porphyritic soil.		On moist woodland.		
Potash	5·23	13·34	24·93	18·45	47·15	45·59	44·80	44·09	44·16	48·53	47·48	36·67	54·02	37·63
Lime	47·70	32·58	18·04	25·48	7·65	9·54	10·81	10·68	8·37	9·42	6·64	10·20	8·14	13·54
Magnesia . . .	1·06	3·70	2·53	2·27	1·08	4·57	2·43	3·01	1·99	0·48	0·86	0·36	0·68	1·94
Sulphuric acid (SO^3) .	. .	. .	3·13	7·92	2·90	2·90	. .	.	3·08	1·36	0·76	1·02	1·22	2·94
Silica	0·70	1·97	0·87	4·27	0·60	1·31	0·58	1·13	0·64	0·16	0·43	0·15	0·37	0·69
Carbonic acid (CO^2) .	37·92	24·16	16·78	12·89	17·64	22·17	21·47	21·58	15·75	17·83	24·61	13·07	27·97	18·88
Phosphoric acid (P^2O^5) .	3·75	14·58	12·32	19·48	14·07	12·94	15·33	13·31	17·55	18·74	3·98	19·15	5·40	15·36
Chloride of potassium .	3·64	9·67	21·40	9·24	8·91	3·88	4·58	6·20	8·46	3·48	15·42	19·38	2·20	9·02
	100·00	100·00	100·00	100·00	100·00	100·00	102·90	100·00	100·00	100·00	100·18	100·00	100·00	100·00
Ash per cent. . .	7·85	1·05	13·38	7·62	11·36	6·65	6·56	6·10	4·39	3·36	7·29	2·26	4·53	1·70
Moisture . . .	54·98	48·45	84·04	75·41	85·21	83·16	83·60	86·67	81·01	52·88	82·70	49·67	81·12	64·00
Percentage of ash soluble in water . . .	11·35	29·21	59·38	39·77	81·16	72·70	72·22	72·70	77·77	77·02	85·37	. .	81·96	31·23

quinovin, and may be regarded as a compound of æscigenin with 2 at. propionic acid:

$$C^{30}H^{50}O^{8} = C^{24}H^{38}O^{4} + 2C^{3}H^{6}O^{2}.$$

This view of its composition is supported by the formation of a compound, $C^{28}H^{44}O^{7}$ [?$C^{28}H^{46}O^{8}$], containing the elements of æscigenin and acetic acid, by the action of chloride of acetyl on æscigenin.

Rochleder considers it probable that æscigenin or its compounds may exist in other plants, and that cyclameïn and digitaliretin may belong to this group of compounds.

The ash of the different parts of the horse-chestnut tree has been analysed by E. Wolff (J. pr. Chem. xliv. 385; Jahresber. 1847–8, p. 1078), for the purpose of determining how the proportion of the different mineral constituents are modified in passing from one organ to another, and how these constituents are distributed throughout the several organs. To eliminate any local character from the results, the organs subjected to examination were selected from trees growing on two very different soils; one a stony porphyritic soil, the other a moist forest soil often overflowed, very rich in vegetable mould, and much more favourable to the growth of the trees than the former. The mineral constituents were extracted by first charring the substance in a muffle heated not quite to redness, and exhausting the charcoal, first with water, then with dilute hydrochloric acid, drying the carbonaceous residue, and incinerating it completely in the muffle. The ash was then likewise exhausted with hydrochloric acid, and the united hydrochloric extracts, the aqueous extract, and the insoluble residue, were separately analysed. The results are given in the table on page 173.

The ash of the wood, bark and leaves of the horse-chestnut has also been analysed by E. Staffel (Ann. Ch. Pharm. lxxvi. 379; Jahresber. 1850, p. 661), chiefly with the view of determining whether the amount of the several inorganic constituents in the plant and its different organs varies with the season of the year. The method of analysis was similar to that adopted by Wolff, excepting that the charcoal was exhausted with water alone.

Ash of Horse-chestnut (Staffel).

	Wood.		Bark.		Leaves.	
	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn
Potash . . .	57·57	17·54	54·96	22·61	46·38	18·17
Lime . . .	5·92	50·99	9·24	61·34	13·17	40·48
Magnesia . . .	4·08	5·17	4·36	3·99	5·15	7·78
Alumina . . .	. .	0·23	. .	0·18	0·41	0·51
Ferric oxide * . .	0·31	0·63	1·66	0·31	1·63	4·69
Sulphuric acid (SO^{3}) .	0·82	. .	. .	1·05	2·45	1·69
Silica . . .	1·80	0·71	0·67	1·06	1·76	13·91
Phosphoric acid ($P^{2}O^{5}$)	19·02	21·73	19·54	6·95	24·40	8·22
Chloride of potassium	10·47	2·98	9·56	2·50	4·65	8·55
	99·99	99·98	99·99	99·99	100·00	100·00
Ash per cent. of dry substance . .	10·908	3·88	8·68	6·57	7·69	7·52
Ash per cent. of fresh substance . .	1:198	1·693	1·342	3·171	1·376	3·288
Moisture in 100 parts of air-dried substance . . .	89·01	49·90	84·45	51·73	82·09	56·27

HORSE-FLESH ORE. A term applied by the Cornish miners to certain varieties of *purple copper*.

HOUGHITE. A hydrated aluminate of magnesium, occurring, as the material of pseudomorphous spinel, near Oxbow, and in Rossie, near Somerville, St. Lawrence county, New York. The crystals are in all conditions, from the pure spinel to octahedrons with rounded edges and pitted or irregular surfaces; it also occurs in flattened nodules. It is perhaps identical with *Völknerite* (*q. v.*). (Dana, ii. 135.)

HOVITE. A mixture of collyrite (i. 1084) with a hydrated carbonate of aluminium and calcium, found in the Upper chalk, in the neighbourhood of Hove, near Brighton. It is very soft and friable, having an earthy fracture and low specific gravity. (J. H. and G. Gladstone, Phil. Mag. [4] xxiii. 461; Jahresber. 1862, p. 743.)

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* With a trace of manganic oxide.

HOWARDITE. A meteoric mineral, described by C. U. Shepard. (Sill. Am. J. [2] vi. 402.)

HUANOKINE. $C^{20}H^{24}N^2O$.—An alkaloïd, isomeric, or perhaps identical, with cinchonine; obtained from *China de Huanoco plana*, a cinchona-bark found in the Huanoco forests, north of Lima (A. Erdmann, Ann. Ch. Pharm. c. 341). The bark is repeatedly exhausted with water containing hydrochloric acid, and the base, precipitated by caustic soda, is purified by repeated solution in acid, and reprecipitation, till it becomes white, and finally by crystallisation from alcohol.

Huanokine crystallises in small colourless prisms, very similar in form to cinchonine. According to H. Hahn (Jahresber. 1858, p. 372), they are monoclinic prisms, exhibiting the faces $\infty P \,.\, \infty P\infty \,.\, oP$. Angle $\infty P : \infty P$ in the clinodiagonal principal section = 71°; $oP : \infty P\infty$ = 110°. Cleavable parallel to oP; less distinctly parallel to $\infty P\infty$. It is tasteless; but has a slight alkaline reaction, stronger in the alcoholic solution, which is also slightly bitter. It melts without decomposition, and solidifies in the crystalline form on cooling: at a stronger heat it sublimes. It is nearly insoluble in water, dissolves in 400 pts. alcohol of 80 per cent. at 17°; and in 110 pts. at the boiling heat; in 600 pts. ether at 17°; and in 470 pts. at the boiling heat. It is said to be a strong febrifuge.

The salts of huanokine are precipitated white by alkalis and alkaline carbonates, yellowish white by tincture of galls, white by mercuric chloride, yellow by chloride of gold.

The *sulphate* is nearly insoluble in water; but dissolves easily in excess of acid; the solution is not fluorescent.—The *hydrochlorate* is very soluble, and crystallises in large colourless prisms having an extremely bitter taste; not fluorescent. According to Hahn (*loc. cit.*) the crystals are rhombic prisms, with the faces $\infty P\infty \,.\, \bar{P}\infty \,.\, P$. Angle $\infty P : \infty P = 30°$.— The *chloroplatinate* also forms rhombic crystals, $\infty P \,.\, \infty\bar{P}\infty \,.\, P$. Angle $\infty P : \infty P = 75°$; angle between the macrodiagonal terminal edges and the principal axis = 132°.— The *tartrate* forms hemihedral rhombic crystals, $\infty P \,.\, \infty\breve{P}\infty \,.\, oP \,.\, \frac{P}{2}$. Angle $\infty P : \infty P. = 138°$; $\frac{P}{2} : \frac{P}{2} = 70°$. (Hahn.)

According to De Vry (J. Pharm. [3] xxxii. 328), huanokine is identical with cinchonine, the differences observed by Erdmann between it and cinchonine having been probably due to admixture of quinidine or cinchonidine. He found that hydriodate of cinchonine agreed perfectly, in external character and in its relations to polarised light, with the hydriodate obtained from huanokine prepared by Erdmann himself.

HUDSONITE. A black mineral from Cornwall, Orange County, New York, near the Hudson River. Specific gravity 3·43 to 3·5. It cleaves like Hedenbergite, and is regarded by Dana as a variety of augite, having a considerable portion of the silica replaced by alumina. The composition is, however, more like that of hornblende. Smith and Brush (Sill. Am. J. [2] xvi. 369) found in it:—

SiO^2	Al^4O^3	Fe^2O	Mn^2O	Ca^2O	Mg^2O	K^2O	Na^2O	Loss by ignition.
38·94	10·41	30·48	0·60	10·36	3·00	2·48	1·66	1·95 = 99·88

Kenngott found that a mineral from Monroe, designated as Hudsonite, was really a hornblende. (*Rammelsberg's Mineralchemie*, p. 996.)

HUMBOLDTILITE. Syn. with MELLILITE.

HUMBOLDTINE. Syn. with OXALITE.

HUMBOLDTITE. Syn. with DATHOLITE.

HUMIC ACID. See ULMIC ACID.

HUMITE. See CHONDRODITE (i. 930).

HUMOPIC ACID. $C^{22}H^{20}O^7$ (?) (Wöhler, Ann. Ch. Pharm. l. 21).—An acid produced, with evolution of ammonia, by heating narcotine to about 220°.

$$C^{22}H^{23}NO^7 = C^{22}H^{20}O^7 + NH^3 \; [?]$$

It is purified by dissolving it in potash, precipitating with hydrochloric acid, re-dissolving in alcohol, and precipitating by water. It is an amorphous, dark-brown substance, insoluble in water and in dilute acids, but dissolves in alcohol with yellowish-red, and in alkalis with yellow colour, the latter solution forming brown gelatinous precipitates with barium- and lead-salts.

Wöhler's analysis of this acid gave 63·0 and 64·5 per cent. carbon, 5·3 and 5·0 hydrogen; whence he suggested the formulæ, $C^{58}H^{22}O^{27}$ and $C^{40}H^{19}O^{14}$. The formula above given (which requires 66·7 per cent. carbon and 5·3 hydrogen) is based upon the formula of narcotine recently established by Matthiessen and Foster (*Gmelin's Handbook*, v. 138). It is probable, however, that the acid has not been obtained pure, and that the decomposition of narcotine by heat may be more complicated than that which is represented by the preceding equation.

HUMOURS OF THE EYE. See Eye (ii. 654).

HUMUS, or *Vegetable Mould*, is the product of the decay of vegetable matter. The fallen leaves, and all the parts of plants which are returned to the soil, either during the life of the plant or after its death, undergo peculiar alterations, the result of which is to transform them into a mass of compounds whose nature has not been exactly ascertained, but which are known to contain a large proportion of carbon. This decay is promoted by the action of air, by moisture, and by a certain degree of heat. It takes place most quickly in those constituents of the plant which are soluble in water, some of the insoluble matters, such as resins and fats, resisting decomposition for a long time, and remaining almost in their original state, so that they may be extracted from the humus by alcohol or ether. The decomposition is also greatly accelerated by the presence of putrifying nitrogenous matters; and this is doubtless one cause of the beneficial effect of animal manure.

Vegetable mould is in a continual state of slow combustion, whereby the organic compounds which it contains are gradually resolved into carbonic acid, water, and ammonia, which, as they are formed, are taken up by the roots and plants: hence the effect of vegetable mould in promoting the growth of plants, and partly also the advantage gained by frequently turning up and pulverising the soil, whereby the access of air and the decomposition of the organic matter are facilitated.

HUNTERITE. The name applied by S. Haughton (Phil. Mag. [4] xvii. 18; Jahresber. 1859, p. 289) to a hydrated silicate of aluminium, having a fatty lustre and the aspect of felspar, found in a coarsely crystalline granite in the neighbourhood of Nágpur in Central India. Specific gravity = 2·319. According to Haughton's analysis, it contains 65·93 per cent. SiO^2, 20·97 Al^4O^3, 0·30 Ca^2O, 0·45 Mg^2O and 11·61 water (= 99·26). This is very nearly the composition of cimolite (i. 984), with which also the mineral agrees nearly in lustre and specific gravity: hence Dana (Sill. Am. J. [2] xxviii. 133), regards it as identical with cimolite.

HUREAULITE. A phosphate of iron and manganese from Hureault, near Limoges, where it occurs in small veins in the granite. It forms translucent crystals belonging to the monoclinic system, having a yellowish- or reddish-brown colour and vitreous lustre. Specific gravity = 2·27. Somewhat softer than felspar; contains, according to the mean of Damour's analyses (Ann. Min. [5] v.), 38·00 per cent. P^2O^5, 41·67 Mn^2O, 7·86 Fe^2O, 11·98 water, and 0·38 quartz &c.; whence the formula $\left.\begin{matrix}\frac{5}{6}Mn^2O\\ \frac{1}{6}Fe^2O\end{matrix}\right\}^5.2P^2O^5 + 5H^2O$; or it may be a double salt consisting of a pyro- and orthophosphate, of the form $M^4P^2O^7.2M^3PO^4.5H^2O$. (*Rammelsberg's Mineralchemie*, p. 330.)

HURIN. An acrid crystalline substance obtained from the juice of *Hura crepitans*. (Boussingault and Rivero, Ann. Ch. Phys. [2] xxviii. 430.)

HURONITE. A mineral from Lake Huron, containing 45·80 SiO^2. 33·92 Al^4O^3, 8·04 Ca^2O, 4·32 Fe^2O, 1·72 Mg^2O and 4·16 water. It forms imperfectly laminated masses, having a light greenish yellow colour and waxy lustre, translucent on the edges. (Handw. d. Chem. iii. 942.)

HVERSALT. Native iron-alum from Iceland. (See Sulphates.)

HYACINTH. See Zircon.

HYÆNANCHE GLOBOSA. (Lamb).—A euphorbiaceous plant, the pericarp of which contains a very acrid poisonous substance, resembling strychnine and the allied poisons in its action. The poisonous substance is uncrystallisable, easily soluble in water and in alcohol; it has neither basic nor acid properties, but cannot be classed among the resins, on account of its solubility in water. The husk of the fruit contains 9·40 per cent. water, 5·36 gypsum, lime, potash, and chlorine; 2·52 wax and chlorophyll; 9·64 tannic acid; 5·64 resin; 15·15 starch, gum, and sugar; 3·99 varnish-like substance, soluble in water and in alcohol; 36·00 cellulose; and lastly, oxalic acid, and substances which can be extracted by strong hydrochloric acid and potash-ley. The seeds give up to ether, 41·06 per cent. of a green-yellow fat oil, then to alcohol 24·13 per cent. of a nearly black, brittle resin, resembling kino; they contain 10·7 per cent. of inorganic matters. (J. B. Henkel, Arch. Pharm. [2] xciv. 16; Jahresber. 1858, p. 532.)

HYALITE. See Opal.

HYALOMELANE. Syn. with Trachylyte.

HYALOPHANE. A barytic felspar resembling adularia, discovered by Sartorius v. Waltershausen (Pogg. Ann. xciv. 134; c. 547) in the dolomite of the Binnenthal in the Valais. It is transparent and colourless when pure, but often milk-white from admixture of sulphate of barium. Hardness between 6 and 7. Specific gravity = 2·77 to 2·83. It forms monoclinic crystals resembling those of adularia, ∞P . oP . +P∞, often with (∞P∞). Angle ∞P : (∞P∞) = 120° 36′; oP : ∞P = 112° 0′; oP : +P∞ = 130° 36′. Cleavage perfect parallel to P∞ (Waltershausen). The analysis of a perfectly limpid specimen by Stockar-Escher (*Kenngott's Uebersicht*, 1856–57, p. 107) gave:

SiO^2	Al^4O^3	Ba^2O	Ca^2O	Mg^2O	K^2O	Na^2O	H^2O	
52·67	21·12	15·05	0·46	0·04	7·82	2·14	0·58	= 99·88;

whence the formula $\left.\begin{matrix}\frac{1}{2}Ba^2O\\ \frac{1}{2}K^2O\end{matrix}\right\}SiO^2 + Al^4O^3.3SiO^2 = \left.\begin{matrix}Ba^{\frac{1}{2}}K^{\frac{1}{2}}\\ (Al^2)'''\end{matrix}\right\}Si^2O^6 = \left.\begin{matrix}\overset{''''}{Si^2}\\ (Ba^{\frac{1}{2}}K^{\frac{1}{2}})'\\ (Al^2)'''\end{matrix}\right\}O^6$;
which is similar to that of andesin (see FELSPAR, ii. 618). (*Rammelsberg's Mineralchemie*, p. 609.)

HYALOSIDERITE. A variety of chrysolite from the Kaiserstuhl mountain in the Breisgau, where it occurs in yellowish and brownish-red crystals. It contains 31·63 SiO^2, 32·40 Mg^2O, 28·49 Fe^2O, 0·48 Fe^4O^3 2·21 Al^4O^3, 2·79 K^2O, and a trace of chromium. To bring it under the formula of chrysolite, $2M^2O.SiO^2$ or M^4SiO^4, it is necessary to suppose that part of the silica is isomorphously replaced by alumina.

HYBLITE. See PALAGONITE.

HYDANTOIC ACID. $C^4H^8N^4O^4$ (?)—An acid produced by the action of potash on allantoïn. On supersaturating the solution with acetic acid, precipitating with acetate of lead, decomposing the lead-salt with sulphuretted hydrogen, and evaporating the filtered liquid, the acid is obtained as an uncrystallisable syrup, deliquescent and insoluble in alcohol. It probably contains the elements of allantoïn *plus* 1 at. water ($C^4H^6N^4O^3.H^2O$). (Schlieper.)

The name hydantoic acid is also applied by Baeyer to an acid formed from hydantoïn by addition of the elements of water: no description of it has yet been given.

HYDANTOÏN. $C^3H^4N^2O^2$. (A. Baeyer, Ann. Ch. Pharm. cxvii. 179.)—A compound belonging to the parabanic acid group, produced from allantoïn by the reducing action of hydriodic acid:

$$\underset{\text{Allantoïn.}}{C^4H^6N^4O^3} + 2HI = \underset{\text{Urea.}}{CH^4N^2O} + \underset{\text{Hydantoïn.}}{C^3H^4N^2O^2} + I^2.$$

Also, together with a small quantity of allanturic acid, by the action of hydriodic acid on alloxanic acid:

$$\underset{\text{Alloxanic acid.}}{C^4H^4N^2O^5} + 2HI = \underset{\text{Hydantoïn.}}{C^3H^4N^2O^2} + CO^2 + H^2O + I^2.$$

It crystallises with great facility in colourless crystals easily soluble in water; tastes slightly sweet, and grates a little between the teeth. It is converted by oxidation into allanturic acid:

$$\underset{\text{Hydantoïn.}}{C^3H^4N^2O^2} + O = \underset{\text{Allanturic acid.}}{C^3H^4N^2O^3}.$$

With water it forms Baeyer's hydantoïc acid.

HYDRACIDS. A term formerly applied to hydrochloric, hydrobromic, hydriodic, hydrofluoric, and hydrocyanic acids, to distinguish them from acids containing oxygen. The distinction is, however, no longer maintained, all acids being now regarded as salts of hydrogen. (See ACIDS.)

HYDRACRYLIC ACID. $C^{12}H^{22}O^{11}$.—An acid produced by the decomposition of iodopropionic acid, when a solution of a salt of that acid is heated to boiling:

$$4C^3H^5IO^2 + 3H^2O = C^{12}H^{22}O^{11} + 4HI.$$

It is most easily prepared by digesting iodopropionic acid with excess of silver-oxide, decomposing the resulting silver-salt with sulphydric acid, and evaporating the filtrate. Hydracrylic acid then remains in the form of a syrup, mixed with slender needles. It is tribasic; nearly all its salts are easily soluble in water, and many of them are decomposed by heat, with formation of acrylic acid:

$$\underset{\text{Hydracrylic acid.}}{C^{12}H^{22}O^{11}} = \underset{\text{Acrylic acid.}}{4C^3H^4O^2} + 3H^2O.$$

The *cupric salt* is a blue-green varnish. The *lead-salt*, $C^{12}H^{19}Pb^3O^{11}$, forms a white, crystalline, deliquescent mass, perfectly insoluble in alcohol, and decomposing when heated to between 150° and 200°. The *silver-salt*, $C^{12}H^{19}Ag^3O^{11}$, is a flocculent mass, becoming dark-coloured and amorphous when dry, easily soluble in water, sparingly in alcohol, insoluble in ether; decomposing below 100°. (Beilstein, Ann. Ch. Pharm. cxxii. 366.)

HYDRAMIDES. A group of tertiary diamides (i. 172), formed by the action of ammonia on certain aldehydes, 2 at. of ammonia uniting with 3 at. of the aldehyde, and 3 at. water being eliminated, as shown by the equation—

$$\underset{\text{Bitter Almond Oil.}}{3C^7H^6O} + 2NH^3 = \underset{\text{Hydrobenzamide.}}{N^2(C^7H^6)^3} + 3H^2O$$

The following are the hydramides at present known:—

Furfuramide	$C^{15}H^{12}N^2O^3$	$= N^2(C^5\overset{\prime\prime}{H}{}^4O)^3$
Hydranisamide . . .	$C^{24}H^{24}N^2O^3$	$= N^2(C^8\overset{\prime\prime}{H}{}^8O)^3$
Hydrobenzamide . . .	$C^{21}H^{18}N^2$	$= N^2(C^7\overset{\prime\prime}{H}{}^6)^3$
Hydrocinnamide . . .	$C^{27}H^{24}N^2$	$= N^2(C^9\overset{\prime\prime}{H}{}^8)^3$
Hydrosalicylamide . . .	$C^{21}H^{18}N^2O^3$	$= N^2(C^7\overset{\prime\prime}{H}{}^6O)^3$
Hydrobromosalicylamide .	$C^{21}H^{15}Br^3N^2O^3$	$= N^2(C^7\overset{\prime\prime}{H}{}^5BrO)^3$
Hydrochlorosalicylamide .	$C^{21}H^{15}Cl^3N^2O^3$	$= N^2(C^7\overset{\prime\prime}{H}{}^5ClO)^3$

Glycosine, $N^2(C^2\overset{\prime\prime\prime}{H}{}^2)^3$, from glyoxal (ii. 919), may also be regarded as a hydramide, or rather hydramine.

The aldehydes of the fatty acids (acetic aldehyde and its homologues) do not appear to yield compounds of this class.

The hydramides are crystalline solids, insoluble in water, soluble in alcohol, not volatile without decomposition, and not possessing alkaline properties; but when left in contact with strong caustic alkalis (Fownes), or when simply raised to a high temperature (Bertagnini), they are converted into isomeric compounds possessing strong basic properties, *e. g.* furfuramide into furfurine, hydrobenzamide into amarine. The difference of constitution between these bases and the corresponding hydramides is not precisely understood; but Borodine has shown that amarine contains a larger number of atoms of replaceable hydrogen than its isomer, hydrobenzamide. (See HYDROBENZAMIDE.)

Some hydramides, *e. g.* hydrobenzamide and hydrosalicylamide, are decomposed by acids, yielding ammonia and the corresponding aldehydes. By sulphydric acid they are converted into sulphuretted aldehydes (thialdides), *e. g.* furfuramide into thiofurfol:

$$\underset{\text{Furfuramide.}}{(C^5H^4O)^3N^2} + 3H^2S = 2NH^3 + \underset{\text{Thiofurfol.}}{3C^5H^4OS.}$$

HYDRANZOTIN. $C^2H^4N^2S^4$. *Disulphide of Sulphocarbammonium, Dihydrosulphuretted Sulphocyanogen* (Zeise, Ann. Ch. Pharm. xlviii. 95; Debus, *ibid.* lxxiii. 27).—When chlorine-water is added by small portions to a solution of sulphocarbamate of ammonium in 5 or 6 pts. of water, the liquid being well shaken, and care being taken to avoid an excess of chlorine, this body is produced, as a flocculent crystalline precipitate, which must be washed with cold water till the wash-water no longer reddens ferric salts, and dried in vacuo. It is also produced by heating an aqueous solution of sulphocarbamate of ammonium, first with a large excess of sulphuric or hydrochloric acid, then with a ferric salt.

Hydranzotin, when first prepared, is colourless, with a nacreous lustre, and inodorous; but after a while it gives off sulphuretted hydrogen. It is very sparingly soluble in *water*, dissolves without alteration in *alcohol*, and is dissolved by *ether* in very large quantity, but with some alteration, the solution reddening litmus. An alcoholic solution of *potash* dissolves a considerable portion of it, yielding a neutral liquid, which, when boiled, yields sulphide of potassium, sulphocyanate of potassium and sulphur.

The same transformation takes place on boiling the solution of the compound in absolute alcohol:

$$C^2H^4N^2S^4 = H^2S + 2CHNS + S.$$

The compound is not decomposed by trituration with oxide of lead, unless the mixture is heated. By *dry distillation* it yields sulphide of carbon, accompanied by a little sulphydric acid, and sulphydrate and sulphocarbonate of ammonium, leaving a small quantity of a black substance. It is not perceptibly decomposed by sulphuric or hydrochloric acid.

HYDRARGAMYL, HYDRARGETHYL, &c. See MERCURAMYL, MERCURETHYL, &c.

HYDRARGYLLITE. See GIBBSITE (ii. 838).

HYDRARGYRUM. Syn. with MERCURY.

HYDRASTINE. An alkaloïd discovered by J. D. Perrins (Pharm. J. Trans. [2] iii. 546) in the root of *Hydrastis Canadensis*, in which it exists to the amount of abou

1½ per cent., together with berberine: it appears also to have been previously noticed in 1851 by Durand (Amer. J. Pharm. xxiii. 112). It is very soluble in dilute mineral acids, which, on the other hand, dissolve berberine but sparingly: it may therefore be conveniently obtained from the alcoholic mother-liquors remaining after the separation of berberine (i. 379). For this purpose, the alcohol is distilled off, and the liquid, largely diluted with water, is cautiously mixed with ammonia till the resulting precipitate, consisting of a dark-coloured resin, no longer disappears on stirring. If the filtrate be then mixed with a slight excess of ammonia, hydrastine is precipitated as a brownish-yellow powder, appearing like starch under the microscope, and gradually becoming crystalline. By repeated crystallisation from alcohol, with help of animal charcoal, it is obtained in colourless, shining, four-sided prisms, becoming dull when dry.

Hydrastine is nearly insoluble in *water*, but dissolves easily in *alcohol*, *ether*, *chloroform* and *benzene*, and may be extracted directly from the pulverised root by heating it in a percolator with either of these solvents, neither of which will dissolve berberine.

Hydrastine melts at a temperature a little above 100°; it has a sharp bitter taste, but does not appear to be poisonous. Strong nitric acid colours it yellowish-brown; with sulphuric acid and chromate of potassium, or peroxide of lead, it assumes a brick-red to carmine-red colour. Its solutions mixed with chlorine-water acquire a blue fluorescence.

The salts of hydrastine are for the most part soluble.

HYDRATES. This term is applied to compounds containing oxygen and hydrogen, the whole or part of which exists, or may be supposed to exist, in the form of water; *e. g.*

Hydrate of chlorine . .	$Cl.5H^2O$	Hydrate of sodium .	$Na^2O.H^2O$
Hydrated chloride of barium	$BaCl.H^2O$	Sulphuric acid . . .	$SO^3.H^2O$
Crystallised sulpharsenate of sodium . .	$2Na^3AsS^4.15H^2O$	Crystallised alum .	$Al^2KS^2O^8.6H^2O$
Hydrate of turpentine .	$C^{16}H^{16}.2H^2O$	Crystallised glucose .	$C^6H^{12}O^6.H^2O$

Hydrated oxides may be regarded either as compounds of water with anhydrous oxides, as in the formulæ of hydrate of sodium and sulphuric acid above given, the water playing the part of an acid in the one case and of a base in the other; or as compounds formed from a simple or complex molecule of water, nH^2O, by the replacement of part (mostly half) of the typic hydrogen by a radicle either positive or negative: thus,

	Basic.	*Acid.*	*Alcoholic.*
Water. H^2O	Hydrate of sodium. $\left.\begin{matrix}Na\\H\end{matrix}\right\}O$	Nitric acid. $\left.\begin{matrix}NO^2\\H\end{matrix}\right\}O$	Ethylic alcohol. $\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O$
$\left.\begin{matrix}H^2\\H^2\end{matrix}\right\}O^2$	Platinic hydrate. $\left.\begin{matrix}Pt''\\H^2\end{matrix}\right\}O^2$	Sulphuric acid. $\left.\begin{matrix}(SO^2)''\\H^2\end{matrix}\right\}O^2$	Glycol. $\left.\begin{matrix}(C^2H^4)''\\H^2\end{matrix}\right\}O^2$
$\left.\begin{matrix}H^3\\H^3\end{matrix}\right\}O^3$	Hydrate of aluminium. $\left.\begin{matrix}(Al^2)'''\\H^3\end{matrix}\right\}O^3$	Orthophosphoric acid. $\left.\begin{matrix}(PO)'''\\H^3\end{matrix}\right\}O^3$	Glycerin. $\left.\begin{matrix}(C^3H^5)'''\\H^3\end{matrix}\right\}O^3$
$\left.\begin{matrix}H^4\\H^4\end{matrix}\right\}O^4$	Stannic hydrate $\left.\begin{matrix}Sn^{iv}\\H^4\end{matrix}\right\}O^4$	Glycero-sulphuric acid. $\left.\begin{matrix}(SO^2)''\\(C^3H^5)'''\\H^3\end{matrix}\right\}O^4$	Triethylenic alcohol. $\left.\begin{matrix}(\overset{\prime\prime}{C^2}H^4)^3\\H^2\end{matrix}\right\}O^4$
$\left.\begin{matrix}H^5\\H^5\end{matrix}\right\}O^5$		Pyrophosphoric acid. $\left.\begin{matrix}(P'''O)^2\\H^4\end{matrix}\right\}O^5$	Tetrethylenic alcohol. $\left.\begin{matrix}(\overset{\prime\prime}{C^2}H^4)^4\\H^2\end{matrix}\right\}O^5$
$\left.\begin{matrix}H^6\\H^6\end{matrix}\right\}O^6$	Ferric hydrate. $\left.\begin{matrix}(Fe^4)^{vi}\\H^6\end{matrix}\right\}O^6$	Glycerotartaric acid. $\left.\begin{matrix}(C^4H^2O^2)^{iv}\\(C^3H^5)'''\\H^5\end{matrix}\right\}O^6$	Pentethylenic alcohol. $\left.\begin{matrix}(\overset{\prime\prime}{C^2}H^4)^5\\H^2\end{matrix}\right\}O^6$
$\left.\begin{matrix}H^7\\H^7\end{matrix}\right\}O^7$			Triglycerin. $\left.\begin{matrix}(\overset{\prime\prime\prime}{C^3}H^5)^3\\H^5\end{matrix}\right\}O^7$

The last three compounds in the third column and the last four in the fourth, afford examples of hydrates in which more than half the typic hydrogen is replaced by an acid or alcoholic radicle: other examples of such hydrates (which may also be regarded as anhydrides, inasmuch as they are formed by dehydration of normal hydrates) will be found under ETHYLENE, HYDRATES of (ii. 576), GLYCERYL, HYDRATES of (ii. 894), GLYCEROTARTARIC ACIDS (ii. 893).

Metallic hydrates retain the elements of water with various degrees of force. Hydrate of copper parts with its water at a very moderate heat; hydrate of calcium, at a strong red heat; while the hydrates of potassium and sodium are not decomposed by the strongest heat that can be applied to them. Hydrated acids likewise exhibit various degrees of stability. Tribasic phosphoric acid, $P^2O^5.3H^2O$ or PH^3O^4, gives off part of its water at a red heat, being converted first into the dibasic acid, $P^2O^5.2H^2O$, and ultimately into the monobasic acid, $P^2O^5.H^2O$, which resists further decomposition. The hydrates of volatile acids exhibit remarkable relations to heat. Under given circumstances of pressure and temperatures, there is for each acid a certain proportion of water which forms a stable compound, a weaker acid under that pressure and temperature giving off water, and a stronger acid giving off acid, till the most stable compound remains behind (Roscoe, Chem. Soc. Qu. J. xiii. 146). See SULPHURIC ACID, NITRIC ACID, CHLORHYDRIC ACID, &c.

The hydrates of the stronger acids and bases may be formed by direct combination of the anhydrous base or acid (anhydride) with water, the combination being sometimes attended with great evolution of heat, as in the case of sulphuric acid, baryta, and lime. In other cases, the hydrate cannot be formed directly, and in others again the union takes place but slowly. Acetic anhydride may be left in contact with water for several days without dissolving in it; but on the application of heat, it gradually dissolves. Among organic acids, it is found that dibasic acids are formed by the direct union of the anhydride and water, and that the hydrate may be decomposed by heat: this is the case with succinic and tartaric acids; whereas the hydrates of monobasic acids, such as acetic acid, cannot be thus decomposed by heat alone. This difference is probably related to the fact, that the molecule of a dibasic acid, like succinic acid, $\left.\begin{matrix}(C^4H^4O^4)''\\H^2\end{matrix}\right\}O^2$, contains a sufficient number of atoms of basic hydrogen to form water; whereas the molecule of a monobasic acid, such as acetic acid, $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$, does not.

The hydrates of lithium, sodium, potassium, barium, strontium, and thallium, are easily soluble in water, forming strongly alkaline solutions; hydrate of calcium is moderately soluble; the other metallic hydrates are insoluble or nearly so; those of magnesium, mercury, lead, and silver are, however, sparingly soluble. The hydrates of the more acid or chlorous radicles are all more or less soluble in water, with the exception of certain organic acids of high atomic weight, such as the higher members of the fatty acid series, palmitic, stearic, cerotic acid, &c.: these bodies dissolve readily in alcohol and in ether. Similar remarks apply to the alcoholic hydrates.

In many hydrated compounds, part or the whole of the oxygen and hydrogen appears actually to exist as water, as in bases, salts, &c., containing water of crystallisation: *e. g.* crystallised *hydrate of barium*, $BaHO.4H^2O$, *crystallised alum* $(SO^4)^2Al^2K.12H^2O$. Water can unite in this manner with salts and other bodies in the most various proportions, sometimes one molecule of the salt being united with several molecules of water, as in the instances above given, and sometimes, though less frequently, one molecule of water with two or more molecules of the salt; sometimes in more complex proportions, as in crystallised *nitrate of strontium*, $2NO^3Sr.5H^2O$.

Water thus united with a salt or other body is for the most part expelled at 100° C.: some salts, however, retain part of their water with greater tenacity than the rest; thus crystallised sulphate of zinc, $Zn^2SO^4.7H^2O$, gives off 6 at. water at 100°, but retains the seventh atom till heated to 238°; sulphate of magnesium, $Mg^2SO^4.7H^2O$, exhibits a similar deportment. Moreover, this last atom of water, which by its greater stability appears to be more intimately united with the salt than the rest, may be replaced by a molecule of another salt, as sulphate of potassium or ammonium:

Crystallised sulphate of zinc . . .	$Zn^2SO^4.H^2O + 6$ aq.
Sulphate of zinc and potassium . .	$Zn^2SO^4.K^2SO^4 + 6$ aq. or $ZnKSO^4 + 3$ aq.

Water united with a salt in this manner is called by Graham, *constitutional water*, to distinguish it from water of crystallisation. Liebig distinguishes these hydrated compounds, *e. g.* $Zn^2SO^4.H^2O$, by the term *halhydrates*.

HYDRAULIC LIMESTONE. See LIMESTONE.

HYDRIDES. This term is applied chiefly to the compounds of hydrogen with metals, alcohol-radicles, and organic-acid-radicles, *e. g.* hydride of copper, Cu^2H; hydride of ethyl, $C^2H^5.H$; hydride of benzoyl, $C^7H^5O.H$.

Metallic Hydrides. A few only of these compounds are known. The most important are the gaseous hydrides of *arsenic* and *antimony*, AsH^3 and SbH^3 (i. 322, 371), formed on the ammonia type. *Phosphoretted hydrogen*, or *phosphamine*, PH^3, belongs to the same class. There is also a solid hydride of arsenic, supposed to have the composition AsH^2, produced when water is electrolysed by a strong current, with metallic arsenic for the negative pole. It is doubtful whether a hydride of *bismuth* exists, analogous to the gaseous arsenides of arsenic and antimony. Hydride of *copper*, Cu^2H or $CcuH$, produced by the action of hypophosphorous acid on aqueous cupric sulphate, is remarkable for its reaction with hydrochloric acid, the products of which are cuprous chloride, $CcuCl$, and free hydrogen (ii. 66). A hydride of *iron* has been obtained by Wanklyn and Carius (Ann. Ch. Pharm. cxx. 69) by acting on ferrous iodide with zinc-ethyl. It is a black metallic powder, which gives off hydrogen when immersed in water.

Hydrides of Alcohol-radicles.—1. Of the radicles C^nH^{2n+1}. These hydrides are the homologues of marsh-gas, or hydride of *methyl*, $CH^3.H$, the lowest term of the series. The hydrides of *ethyl*, *trityl*, and *tetryl* are gaseous at ordinary temperatures; the rest, up to $C^{15}H^{32}$, the highest yet obtained, are liquids of more or less disagreeable odour, burning with a slightly smoky flame, and regularly increasing in specific gravity, vapour-density, and boiling-point, as their atomic weights become greater. The highest terms of the series will doubtless be found to be solid waxes and paraffins.

Hydride of *methyl* (marsh-gas) is produced by the putrefaction and dry distillation of organic bodies, and by distilling acetic acid or acetone with excess of potash (i. 12). Hydride of *ethyl* is obtained by the decomposition of ethyl itself, which under certain circumstances splits up into this compound and ethylene (ii. 565):

$$2C^2H^5 = C^2H^5.H + C^2H^4;$$

also when iodide of ethyl is decomposed by zinc in presence of water:

$$2C^2H^5I + H^2O + Zn^4 = 2(C^2H^5.H) + Zn^4I^2O.$$

Hydride of *tetryl*, $C^4H^9.H$, is produced by heating tetrylic alcohol with chloride of zinc, and hydride of *amyl*, $C^5H^{11}.H$, together with several of its higher homologues, by similar treatment of amylic alcohol (p. 147).

Hydride of amyl and some of its homologues are also contained, together with other hydrocarbons, in the light oils resulting from the distillation of Boghead coal (Gr. Williams, Phil. Trans. 1857, p. 737; Jahresber. 1857, p. 437.—Chem. Soc. J. xv. 130), and of Wigan cannel coal (Schorlemmer, Chem. Soc. J. xv. 419): for the mode of separating them, see p. 146. Many of these alcoholic hydrides are also contained in American petroleum or earth-oil (which indeed appears to consist almost entirely of them), hydride of *hexyl*, C^6H^{14}, constituting the principal portion (Pelouze and Cahours, Ann. Ch. Pharm. cxxiv. 289; cxxvii. 196; cxxix. 87). They are separated by fractional distillation, and purified by successive treatment with sulphuric acid and carbonate of sodium, desiccation with anhydrous chloride of calcium, distillation over sodium, and final rectification. In this manner, Pelouze and Cahours have obtained twelve of these hydrides, included under the general formula C^nH^{2n+2}, from hydride

Specific Gravities and Boiling Points of Alcoholic Hydrides, C^nH^{2n+2}.

	Specific gravities.			Boiling points.		
	Pelouze and Cahours.	Schorlemmer.	Wurtz.	Pelouze and Cahours.	Schorlemmer.	Wurtz.
Hydrides of						
Tetryl C^4H^{10} .	. .	. .	. .	little above 0°		
Amyl C^5H^{12} .	0·628 at 17°	0·636 at 17°	. .	30°	39°— 40°	28°— 30°
Hexyl C^6H^{14} .	0·669 „ 16	0·678 „ 15·5	. .	68	68 — 70	60 — 64
Heptyl C^7H^{16} .	0·699 „ 15	0·709 „ 17·5	. .	92— 94	98 — 99	
Octyl C^8H^{18} .	0·726 „ 15	0·719 „ 17	0·728 at 0°	116—118	119 —120	115 —118
Nonyl C^9H^{20} .	0·741 „ 15	. .	. .	136—138	. .	134 —137
Decatyl $C^{10}H^{22}$.	0·757 „ 15	. .	0·753 „ 0	160—162	. .	155 —157
Endecatyl $C^{11}H^{24}$	0·765 „ 16	. .	. .	180—184		
Dodecatyl $C^{12}H^{26}$	0·776 „ 20	. .	. .	196—200		
Tridecatyl $C^{13}H^{28}$	0·792 „ 20	. .	. .	216—218		
Tetradecatyl $C^{14}H^{30}$ . .	. .	. .	. .	236—240		
Pentadecatyl $C^{15}H^{32}$ . .	. .	. .	. .	255—260		

of tetryl, C^4H^{10}, boiling at a few degrees above 0°, to hydride of pentadecatyl, $C^{15}H^{32}$, boiling between 255° and 260°. The oil also yields a quantity of liquid boiling above 300°, and doubtless containing some of the higher terms of the same series. Moreover, in boring for it, large quantities of gas escape, exhibiting the characters of marsh-gas: hence it is probable that, in the great geological changes which have given rise to the separation of this remarkable liquid, the whole series of homologous alcohol-hydrides C^nH^{2n+2} has been produced, from marsh-gas up to the highest paraffins.

The preceding table (p. 181) exhibits the specific gravities and boiling-points of the alcoholic hydrides obtained from these several sources. The vapour-densities have also been determined in all cases, and found to agree nearly with those calculated from the respective formulæ for a condensation to 2 volumes. Wurtz's determinations were made on the hydrides obtained by the decomposition of amylic alcohol; Schorlemmer's, on those from cannel-naphtha; those of Pelouze and Cahours, on the hydrides from American petroleum.

These alcoholic hydrides are very stable compounds. They are little, if at all, acted upon by fuming *nitric acid*, strong *sulphuric acid*, or *bromine*; but *chlorine* converts them all into the corresponding alcoholic chlorides $C^nH^{2n+1}Cl$.

Each alcoholic hydride of the series $C^nH^{2n+1}.H$ (except hydride of methyl) is identical in composition with a radicle, simple or mixed, belonging to the same series: thus—

Hydride of	Ethyl $C^2H^5.H$	=	Methyl	$CH^3.CH^3$
„	Trityl $C^3H^7.H$	=	Methyl-ethyl	$CH^3.C^2H^5$
„	Tetryl $C^4H^9.H$	=	Ethyl	$C^2H^5.C^2H^5$
„	Amyl $C^5H^{11}.H$	=	Ethyl-trityl	$C^2H^5.C^3H^7$
		=	Methyl-tetryl	$CH^3.C^4H^9$

and generally:

$$C^{2m}H^{4m+1}.H = C^m H^{2m+1}. C^mH^{2m+1}$$

$$C^{2m+1}H^{4m+3}.H = C^mH^{2m+1}. C^{m+1}. H^{2m+3}$$

The question, therefore, arises: are the members of the two series, the alcohol-radicles and their hydrides, identical or only isomeric? Soon after the isolation of the alcohol-radicles by Frankland and Kolbe, in 1849, Laurent and Gerhardt pronounced the opinion that these compounds were the homologues of marsh-gas. This view has not been generally received as correct (see ALCOHOL-RADICLES i. 96); but recently, Schorlemmer (Chem. Soc. J. xv. 425) has endeavoured to solve the question by examining the products obtained by the action of chlorine on the radicles and their isomeric hydrides. He finds that ethyl-amyl, $C^2H^5. C^5H^{11}$, treated with chlorine, yields a chloride, $C^7H^{15}Cl$, agreeing in composition, as well as in boiling point and other physical properties, with that which is produced by the action of chlorine on hydride of heptyl (p. 144). From amyl, $C^{10}H^{22}$, Schorlemmer obtained, in like manner, a chloride, $C^{10}H^{21}Cl$, boiling at about 200°, which he regards as identical with that which Wurtz obtained by the action of chlorine on hydride of decatyl, $C^{10}H^{21}.H$. From these results, Schorlemmer concludes that no chemical difference exists between the alcoholic hydrides and the radicles, at least among the higher members of the series.

2. *Hydrides of the Alcohol-radicles* C^nH^{2n-7}.—Two compounds of this series are known, viz:—

Hydride of Phenyl (Benzene) $C^6H^6 = C^6H^5.H$
Hydride of Benzyl (Toluene) $C^7H^8 = C^7H^7.H$

Both these hydrides are contained in the light oils obtained by the distillation of coal. When treated with strong nitric acid, they yield substitution-products, in the form of heavy oils, the formation of which affords the means of separating these hydrocarbons from those of other series with which they may be mixed (p. 146). The preparation and properties of these hydrides have already been fully described (i. 542, 573).

The hydrides of alcohol-radicles of other series have not yet been obtained.

Hydrides of Acid-radicles: The aldehydes, referred to the hydrogen-type HH, constitute this class of compounds, *e.g.* acetic aldehyde, $C^2H^4O = C^2H^3O.H$; benzoic aldehyde (bitter-almond oil), $C^7H^6O = C^7H^5O.H$ (see ALDEHYDES, i. 110).

HYDROALOETIC ACID. An acid formed from aloetic or chrysammic acid by the action of water and stannous chloride. A dark violet powder is then produced, which at 120° contains, according to Mulder, $SnO^2.C^{14}H^4N^2O^{11}$. This stannic salt, treated with potash, gives off ammonia and assumes a blue-violet colour; and when heated with strong nitric acid, gives off nitrous fumes, turns red, and yields, first aloetic acid, then, after longer boiling, chrysammic acid (Mulder, Ann. Ch. Pharm. lxxii. 265).

HYDROAPATITE. A hydrated phosphate of calcium, containing fluorine, found in milk-white, translucent, warty concretions, in clefts of a ferruginous-argillaceous rock, imbedded in a black slate, near St. Girons (Ariège) in the Pyrenees. It scratches fluor-spar, but is scratched by steel. Specific gravity = 3·16. It contains

40·00 per cent. P^2O^5, 52·35 Ca^2O, 3·36 F, and 5·30 water, together with 6·43 ferric phosphate, agreeing nearly with the formula $6Ca^3PO^4.2CaF.3H^2O$. (Damour, Ann. Min. [5] x. 65; Jahresber. 1856, p. 874.)

HYDROBENZAMIDE. $C^{21}H^{18}N^2$. *Tribenzylene-diamide, Hydride of Azobenzoyl.* (Laurent, Ann. Ch. Phys. [2] lxii. 23; lxvi. 18; [3] i. 300.—Bertagnini, Ann. Ch. Pharm. lxxxviii. 127.)—This compound, which may be regarded as a tertiary diamide, $N^2(C^7H^6)^{\prime\prime 3}$, in which the hydrogen is completely replaced by the diatomic radicle benzylene, is produced by the action of ammonia on hydride of benzoyl (bitter almond oil). When rectified bitter almond oil (boiling at 180°) is left in contact with aqueous ammonia for a few days, or for only six or eight hours if the liquid be previously heated to the boiling point of the ammoniacal solution, a crystalline mass is formed, which must be broken up, washed rapidly with ether to remove adhering oil, and then dissolved in boiling alcohol, which leaves undissolved a number of secondary products resulting from the action of the ammonia on hydrocyanic acid contained in the bitter almond oil. According to Ekman (Ann. Ch. Pharm. cxii. 151), hydrobenzamide may be obtained in fine crystals by mixing bitter almond oil with an equal volume of ether and strong aqueous ammonia, and leaving the mixture at rest.

Hydrobenzamide separates from its alcoholic solution in colourless octahedrons with a rhombic base, truncated on their longer lateral edges. Angles of the terminal edges, 130° and 122°; angles of the lateral edges, 84° 50′. It is insoluble in water, very soluble in alcohol and ether. The crystals are destitute of taste and odour, but the alcoholic solution has a taste of burnt almonds. The crystals melt at 110°, forming a thick oil, which has a sweet taste, and solidifies after a while to an opaque brown mass.

Decompositions.—1. Hydrobenzamide, when heated in the air, takes fire, and burns with a not unpleasant odour (Laurent).—2. Between 120° and 130° it changes in three or four hours into amarine (Bertagnini).—3. By *dry distillation*, it yields lophine and a strong-smelling volatile oil, leaving a small quantity of carbonaceous matter (Laurent).—4. When the alcoholic solution is continuously boiled, ammonia escapes, and on evaporating the alcohol, bitter almond oil remains (Laurent).—5. Boiled with aqueous *chromic acid*, it yields a large quantity of benzoic acid (Fownes, Phil. Trans. 1845, 263).—6. With *acids*, even at ordinary temperatures, it yields bitter almond oil and the ammonia-salt of the acid (Laurent, Fownes).—7. Boiled with *potash-ley*, it changes gradually and without perceptible decrease of weight, into amarine, only a faint odour of bitter almond oil being evolved (Fownes). Boiled with alcoholic potash, it gives off a small quantity of ammonia and bitter almond oil (Laurent).—8. When it is fused with *hydrate of potassium*, the mass becomes first light yellow, then dark yellow, and ultimately brown and black; and if slowly heated, gives off nothing but ammonia: if the heat be continued, there is given off, besides ammonia, a mixture of about 4 vol. hydrogen gas to 1 vol. carburetted hydrogen. The black residue contains carbonate and cyanide of potassium, benzostilbin, benzolone, and a small quantity of a yellow oil, which thickens and becomes viscid on exposure to the air; the mass, which has then become dark yellow, contains nothing but benzostilbin and a considerable quantity of the yellow oil (Rochleder, Ann. Ch. Pharm. lxi. 89).—9. Heated with *potassium*, it yields a red fusible mass and a small quantity of charcoal (Laurent).—10. When *sulphydric acid* is passed through the alcoholic solution, sulphide of benzylene is produced (Cahours).—11. A solution of hydrobenzamide in absolute alcohol mixed with a solution of *sulphurous anhydride* in absolute alcohol, deposits, after a while, a white precipitate of sulphite of benzoyl and ammonium, $C^7H^5(NH^4)SO^3$, and the remaining solution yields by distillation, first alcohol, then diethyl-benzylenic ether, $\left.\begin{matrix}(C^7H^6)''\\(C^2H^5)^2\end{matrix}\right\}O^2$ (R. Otto, Ann. Ch. Pharm. cxii. 305).—12. When hydrobenzamide is saturated with *hydrochloric acid gas*, a compound free from nitrogen slowly volatilises, whilst a non-volatile azotised compound remains behind, which is not altered by ether, but is dissolved by alcohol, with separation of sal-ammoniac. This compound (hydrochlorate of hydrobenzamide) is resolved by water into sal-ammoniac and hydride of benzoyl:

$$C^{21}H^{18}N^2.2HCl + 3H^2O = 2NH^4Cl + 3C^7H^6O,$$

and by absolute alcohol into sal-ammoniac and diethyl-benzylenic ether:

$$C^{21}H^{18}N^2.2HCl + 6C^2H^6O = 2NH^4Cl + 3\left[\left.\begin{matrix}(C^7H^6)''\\(C^2H^5)^2\end{matrix}\right\}O^2\right].$$

(Ekman, Ann. Ch. Pharm. cxii. 151; Jahresber. 1859, p. 317.—Lieke, ibid. 318).

Hydrochlorate of hydrobenzamide, heated to 160°—230°, yields, besides hydrochloric acid, an oily distillate, containing benzonitrile and chloride of benzyl, C^7H^7Cl (i. 573), and leaves a red-brown residue, which is separated, by digestion with alcohol at ordinary temperatures, into a brown solution (A) and yellow flocks. The latter dissolve in a mixture of alcohol and chloroform, forming a solution which deposits two modifications of lophine, $C^{21}H^{16}N^2$; the one crystallising in needles which melt at 230°, the other in needles which melt at 170° (see LOPHINE). The brown solution (A) yields, first, the two modifications of lophine just mentioned; secondly, a base, probably amarine, melting at 90°; thirdly, a base, $C^{21}H^{20}N^2$, which melts at 100°, forms an oxalate, $C^{21}H^{20}N^2.C^2H^2O^4$, crystallising from alcohol in nacreous laminæ, and a platinum-salt, $C^{21}H^{20}N^2.HCl.PtCl^2.2H^2O$, in microscopic prisms; fourthly, another modification of the same base, whose platinum-salt is anhydrous; and fifthly, an oily base, $C^{14}H^{20}N^2$, forming a hydrochlorate, which melts at 220°, dissolves easily in water and alcohol, and crystallises in six-sided prisms. (Ekman, *loc. cit.*—Kühn, N. Jahrb. Pharm. xvi. 292; Jahresber. 1861, p. 404.)

13. Hydrobenzamide heated with 2 at. *iodide of ethyl* to 80°—100°, yields a dark-brown viscid mass, which, after purification by solution in alcohol, precipitation by water, &c., is found to consist of di-iodide of tribenzylene-diethyl-diammonium $[(\overset{\prime\prime}{C^7}H^6)^3(C^2H^5)^2N^2]''I^2$; and the alcoholic solution of this iodide, treated with oxide of silver or hydrate of lead, yields the base $C^{25}H^{28}N^2O = [(C^7\overset{\prime\prime}{H^6})^3(C^2H^5)^2N^2]O$. This base, again treated with iodide of ethyl, does not yield any distinct compound. (Borodine, Ann. Ch. Pharm. cv. 257.)

Amarine, isomeric with hydrobenzamide, behaves differently with iodide of ethyl; yielding hydriodate of diethylamarine, $C^{21}H^{16}(C^2H^5)^2N^2.HI$, from which, by heating the potash, diethylamarine itself, $C^{21}H^{16}(C^2H^5)^2N^2$, may be obtained; and this base, again treated with iodide of ethyl, yields another base, which forms crystalline salts, and appears to contain a larger proportion of ethyl. This base is likewise acted upon by iodide of ethyl, yielding a hydriodate just like the former. Hence Borodine concludes that amarine contains at least 3 at. H, replaceable by ethyl, and represents it provisionally by the formula $N\left\{\begin{matrix}N(C^7H^6)^3H.\\H^2\end{matrix}\right.$

Chloride of Hydrobenzamide, $C^{21}H^{18}N^2Cl^2$ (Th. Müller, Ann. Ch. Pharm. cxi. 144; Jahresber. 1859, p. 315), is produced by passing dry chlorine gas over hydrobenzamide, which then takes up 19·5 per cent. chlorine, and melts to a viscid yellow liquid. It is decomposed by water, yielding sal-ammoniac, hydrochloric acid, and an oily mixture of hydride of benzoyl and benzonitrile, boiling between 180° and 199°:

$$\underset{\text{Chloride of hydrobenzamide.}}{C^{21}H^{18}N^2Cl^2} + 2H^2O = \underset{\text{Hydride of benzoyl.}}{2C^7H^6O} + \underset{\text{Benzonitrile.}}{C^7H^5N} + NH^4Cl + HCl.$$

By anhydrous ether it is resolved into sal-ammoniac, and a mixture of benzonitrile with an oily body which boils at 183°, and has the composition of chlorohydrobenzamide (see below), but differs from that substance by its ready decomposibility by water into benzonitrile and hydride of benzoyl.

Chloride of hydrobenzamide heated to 180°—200° is resolved into hydrochloric acid, chlorohydrobenzamide, $C^{21}H^{17}ClN^2$, which distils over as a colourless oil, and a residue which solidifies on cooling, and is resolved, by successive treatment with water, ether, and alcohol, into the following compounds:

The *aqueous* solution deposits on cooling a white powder, which separates from alcohol in hard granular crystals, consisting of $C^{28}H^{23}ClN^2.HCl$ or $C^{28}H^{24}N^2.Cl^2$; from water the same compound crystallises with 1 at. H^2O. Ammonia added to the solution throws down [? as a hydrate] the base $C^{28}H^{24}N^2 = N^2(C^7\overset{\prime\prime}{H^6})^4$, which may be called tetrabenzylene-diammonium. The chloroplatinate, $C^{28}H^{24}Cl^2N^2.PtCl^2$, is easily soluble.

The *ethereal* solution deposits crystalline needles insoluble in water, subliming at 300°, and having the composition $C^{28}H^{21}N^2$.

The *alcoholic* solution yields crystals insoluble in water and in ether, and containing, when dried over oil of vitriol, $C^{28}H^{23}N^2.HCl.2H^2O$. If the base be separated from this salt by ammonia, and redissolved in hydrochloric acid, the solution yields by evaporation a basic hydrochlorate, $2C^{28}H^{22}N^2.HCl.2H^2O$. The chloroplatinate, which is light yellow, contains $C^{28}H^{22}N^2.HCl.PtCl^2$ (platinum, by experiment, 17·4 per cent.; by calculation, 17·9).

Chlorohydrobenzamide. $C^{21}H^{17}ClN^2$. (Th. Müller, *loc. cit.*)—When chloride of hydrobenzamide is heated to 180°—200°, this compound distils over as a colourless oil, heavier than water, and having a pungent odour of chlorine and benzonitrile together. It dissolves easily in alcohol and in ether, and is slowly decomposed by water, with formation of hydrochloric acid. When left in contact, for 24 hours, with a mixture of *nitric* and *sulphuric acids*, it forms a solution from which water throws down crystallisable nitrobenzonitrile, $C^7H^4(NO^2)N$.

Chloronitro-hydrobenzamide. $C^{21}H^{16}Cl(NO^2)N^2$. (Müller, *loc. cit.*)—This compound is formed when chlorohydrobenzamide is left for 24 hours in contact with strong *nitric acid*, and is precipitated by water from the acid solution, as an oily very pungent liquid. It is soluble in alcohol, and the solution is decomposed by sulphide of ammonium, yielding benzonitrile and sulphobenzamide:

$$\underset{\text{Chloronitro-hydrobenzamide.}}{C^{21}H^{16}Cl(NO^2)N^3} + 3H^2S = \underset{\text{Benzonitrile.}}{2C^7H^5N} + \underset{\text{Sulphobenzamide.}}{C^7H^7NS^2} + 2H^2O + HCl + S^2.$$

HYDROBENZILE. $C^{14}H^{12}O$. (Zinin, J. pr. Chem. xxxiii. 35.)—A product of the action of sulphide of ammonium on benzile ($C^{14}H^{10}O^2$). It is insoluble in water, soluble in alcohol and ether, and crystallises from these solutions in the shape of concavo-convex lenses. The crystals melt at 47°, forming a colourless liquid, which distils without alteration, and solidifies in a crystalline mass at 42°. They have the smell of bitter almonds, and a saccharine pungent taste. They dissolve readily in sulphuric acid, and are precipitated therefrom by water. They are slowly attacked by chlorine, and not sensibly altered by boiling potash.

HYDROBENZOÏN. $C^{14}H^{14}O^2$. (Zinin, Ann. Ch. Pharm. cxxiii. 125.)—A compound produced by the action of nascent hydrogen on benzoyl-hydride (bitter almond-oil), and containing the elements of 2 molecules of that compound ($C^{14}H^{12}O^2$), and 1 molecule of hydrogen, H^2. To prepare it, 4 pts. of bitter almond oil free from prussic acid are dissolved in 6 pts. alcohol of 85 per cent.; the solution is mixed with 4 pts. alcohol previously saturated with hydrochloric acid gas; and one pt. of finely-granulated zinc is carefully added, so that it may dissolve without perceptible evolution of hydrogen. When the reaction is finished, the liquid is heated to the boiling point, mixed after cooling with a small quantity of ether (to remove a body which adheres to the zinc and retards the action) and with 1 pt. more of alcohol saturated with hydrochloric acid gas, then heated to complete the reaction, and mixed with a quantity of water three or four times as great as that of the bitter almond oil taken. Hydrobenzoïn then separates as an oily body, which soon solidifies in a crystalline mass, and may be purified by washing in water, pressure between bibulous paper (to remove an acrid oil), and recrystallisation from alcohol (or if somewhat impure, previously from ether). It is thus obtained in large rhombic plates, which melt at 130°, and boil above 300°. When gently heated with 2 pts. nitric acid of specific gravity 1·36, it is converted, without any evolution of red vapours or formation of secondary products, into pure benzoïn; with stronger nitric acid, benzil is obtained. It is not attacked by potash, either aqueous or alcoholic, even at the boiling heat.

HYDROBERBERINE. $C^{20}H^{21}NO^4$. (Hlasiwetz and Gilm. Ann. Ch. Pharm. Suppl. ii. 191; Rép. Chim. pure, 1863, p. 426.)—A base produced by the action of nascent hydrogen on berberine, as first observed by Hlasiwetz (Rép. Chim. pure, 1862, p. 367). It is obtained by boiling in a flask, provided with a condensing tube to cause the vapours to flow back, a mixture of 6 pts. berberine, 100 pts. water, 10 pts. distilled sulphuric acid, 20 pts. glacial acetic acid, a quantity of granulated zinc, and a few pieces of platinum foil. The liquid gradually loses its colour, and as soon as the froth exhibits a wine-yellow colour, which it does after boiling for an hour or two, the action is stopped, the liquid filtered, any crystalline deposits that may have formed are dissolved in dilute sulphuric acid, and an excess of ammonia is added after cooling. Hydroberberine is then obtained as a bulky yellowish deposit, which must be collected on a filter, washed, dried at a gentle heat, then pulverised, boiled in alcohol, and purified by repeated crystallisation from alcohol. Instead of precipitating the base by ammonia, it may be advantageously obtained as a hydrochlorate, by adding common salt to the original solution. The hydrochlorate is then almost wholly deposited in the form of a crystalline powder.

Hydroberberine may also be prepared by acting on berberine with sodium-amalgam, but it is then yellow and more difficult to purify.

Hydroberberine is deposited from a hot alcoholic solution, in small shining granular crystals, or flattened needles, which are colourless or slightly yellowish, and appear to belong to the monoclinic system. It differs from berberine, $C^{20}H^{17}NO^4$ (the formula lately determined by Perrins, Chem. Soc. J. xv. 339), by four additional atoms of hydrogen, and may be reconverted into that compound by the action of nitric acid. On dissolving it in a mixture of equal volumes of hydrochloric acid and alcohol, and dropping in nitric acid diluted with alcohol, the liquid becomes coloured, and deposits crystals of hydrochlorate of berberine.

Hydrochlorate of Hydroberberine. $C^{20}H^{21}NO^4.HCl$.—Crystals of hydroberberine spread upon a watch-glass, under a bell-jar within which hydrochloric acid is evolved, are converted into a white powder, consisting of the hydrochlorate, soluble in warm water, and crystallising in laminæ on cooling. The salt may also be obtained by dissolving the base in hot hydrochloric acid; the solution on cooling forms a jelly, which is gradually transformed into crystals. It is more soluble in alcohol than in water. Its solutions yield copious precipitates with *chloride of platinum;* from a warm alcoholic solution, the platinum-salt is more gradually deposited in orange-yellow crystalline grains, consisting of $C^{20}H^{21}NO^4.HCl.PtCl^2$.

The *hydrobromate* and *hydriodate* are white, crystalline, and very slightly soluble.

The *nitrate*, which is also crystalline and very slightly soluble, is seldom obtained pure by dissolving the base in nitric acid, because the acid decomposes it; better by mixing a hot, very dilute solution of the sulphate with nitrate of sodium.—The *oxalate* crystallises in small rhombic plates, the *phosphate* in fine rhombic plates.

Sulphates of Hydroberberine. The neutral sulphate, $(C^{20}H^{21}NO^4)^2.H^2SO^4$, is obtained by dissolving an excess of the base in very dilute sulphuric acid. The liquid then deposits needles which fill it entirely, and after being expressed and purified by crystallisation, are very soluble in water, and contain a certain quantity of water, which they lose by exposure to the air; they likewise invariably contain a little free acid.

When the base is dissolved in a slight excess of acid, large transparent rhombohedrons are obtained, approaching nearly to the cube; they give off water when exposed to the air, and cannot be dissolved in water without decomposition. They appear to be a mixture of the neutral and acid sulphates, containing $4C^{20}H^{21}NO^4.3SH^2O^4.4H^2O$, or

$$\left.\begin{matrix}(C^{20}H^{21}NO^4)^2.SH^2O^4\\ 2(C^{20}H^{21}NO^4.SH^2O^4)\end{matrix}\right\}.4H^2O.$$

A moderately dilute solution of this salt mixed with excess of sulphuric acid becomes turbid and deposits small mammellated crystals, or a resinous mass, which gradually changes into crystals of the acid salt, $C^{20}H^{21}NO^4.SH^2O^4$, which may be purified by recrystallisation from alcohol.

Tartrate of Hydroberberine forms mammellated groups of needles.

Ethyl-hydroberberine. $C^{22}H^{25}NO^4 = C^{20}H^{20}(C^2H^5)NO^4$.—Hydroberberine heated for some hours in a water-bath with an excess of iodide of ethyl, yields a pasty mass, which when taken up by alcohol, forms tufts of yellow rhomboïdal prisms, consisting of hydriodate of ethyl-hydroberberine, $C^{22}H^{25}NO^4.HI$, very soluble in water, and containing water of crystallisation, which they give off entirely at 100°. The mother-liquors of the preparation still yield small quadrangular laminæ of another substance, the admixture of which with the first crystals must be avoided.

HYDROBORACITE. *Hydrated Borate of Calcium* and *Magnesium.* $\left.\begin{matrix}3Ca^2O\\ 3Mg^2O\end{matrix}\right\}8B^2O^3.18H^2O$.—Resembles fibrous and foliated gypsum. Colour white with spots of red, from iron. Translucent in thin plates. Melts before the blowpipe to a clear glass, tinging the flame slightly green and not becoming opaque. Heated in a tube it yields water. It is slightly soluble in water, the liquid having a faint alkaline reaction. It dissolves readily in nitric and hydrochloric acids. It was found by Hess (Pogg. Ann. xxxi. 49) in a collection of Caucasian minerals.

HYDROBOROCALCITE. Syn. with BOROCALCITE.

HYDROBROMIC ACID. See BROMIDE OF HYDROGEN (i. 672).

HYDROBRYOTIN. $C^{42}H^{74}O^{16}$.—An amorphous substance, insoluble in ether, but soluble in alcohol, produced by the decomposition of bryonin (i. 685).

HYDROBUCHOLZITE. See KYANITE (p. 449).

HYDROCALCITE. Hydrated carbonate of calcium, $Ca^2CO^3.5H^2O$. Found in small rhombohedral crystals, forming an incrustation on wood under water. (See CARBONATES.)

HYDROCARBONS. Compounds consisting of carbon and hydrogen only. The number of bodies of this class at present known is very great, but the most important of them may be arranged in the following groups:

1. Alcohol-radicles . .	$(C^nH^{2n+1})^2$	homologous with	Methyl $(CH^3)^2$
2. Hydrides of alcohol-radicles . . .	C^nH^{2n+2}	,,	Marsh-gas (CH^4)
3. Olefines . . .	C^nH^{2n}	,,	Ethylene or Olefiant gas (C^2H^4)
4. Hydrocarbons . .	C^nH^{2n-2}	,,	Acetylene (C^2H^2)
5. Camphenes or Terebenes	C^nH^{2n-4}	isomeric with	Turpentine, $C^{10}H^{16}$
6. Hydrocarbons . .	C^nH^{2n-6}	homologous with	Benzene (C^6H^6)
7. Hydrocarbons . .	C^nH^{2n-12}	,,	Naphthalene, $C^{10}H^8$

The most fruitful source of hydrocarbons is the dry or destructive distillation of organic bodies, the nature of the products varying according to the temperature at which the decomposition takes place. Thus, coal when distilled at a bright red, as for the production of illuminating gas, yields hydrocarbons belonging to the second, third, fourth and sixth of the above groups, together with a considerable quantity of naphthalene; but when distilled at the lowest temperature at which complete decomposition can take place, it yields liquid hydrocarbons belonging chiefly to the second and third groups, together with a large quantity of paraffin, which probably also belongs to the second group. The slow decomposition of organic matters buried beneath the surface of the earth has also yielded large quantities of hydrocarbons belonging to the second group, as shown by the enormous quantities of petroleum found in certain parts of North America, which, as already observed (p. 181), consists almost wholly of alcoholic hydrides of the general formula C^nH^{n+2}.

The olefines, C^nH^{2n}, are produced by the dehydration of alcohols of the series $C^nH^{2n+2}O$, as by heating these alcohols with strong sulphuric acid or chloride of zinc, each alcohol then yielding the corresponding olefine, according to the equation $C^nH^{2n+2}O - H^2O = C^nH^{2n}$.

The reaction, however, at least in the case of some of the higher alcohols, is much more complicated than this equation would imply, resulting in the formation, not only of the olefine corresponding to the alcohol decomposed, but likewise of several of its homologues, and of the corresponding alcoholic hydrides; thus Wurtz, by distilling amylic alcohol with chloride of zinc, has obtained, not only amylene, C^5H^{10}, but likewise all its homologues up to decatylene or diamylene, $C^{10}H^{20}$, together with the corresponding alcoholic hydrides.

The lowest term of the olefine series, viz. methylene, CH^2, is not known in the free state. Ethylene, C^2H^4, tritylene or propylene, C^3H^6, and tetrylene, C^4H^8, are gaseous at ordinary temperatures; amylene, C^5H^{10}, and its higher homologues up to decatylene, $C^{10}H^{20}$, and cetylene, $C^{16}H^{32}$, are liquid at ordinary temperatures, their boiling points rising as their molecular weights increase. Cerotene, $C^{27}H^{54}$, and melissene, $C^{30}H^{60}$ are waxy solids, the former melting at 57° or 58°, the latter at 62°.

The more volatile olefines are remarkable for the facility with which they unite with *chlorine*, *bromine*, and *iodine*, forming compounds homologous with, or analogous to, Dutch liquid, $C^2H^4Cl^2$. This property affords an easy mode of separating these olefines from any gaseous mixture in which they may be present: for on passing the gaseous mixture through a bottle containing bromine, the olefines are absorbed and converted into heavy oily liquids (hence their name), while the other hydrocarbons in the mixture are unaffected.

The olefines unite very readily with *sulphuric anhydride;* and this property likewise affords an easy mode of separating them from gaseous mixtures: thus, if a ball of coke or pumice impregnated with Nordhausen sulphuric acid be passed up into a mixture of ethylene-gas with marsh-gas, hydrogen, carbonic oxide, &c., the ethylene will be absorbed, while the other gases will remain behind.

The volatile olefines also unite readily with strong *sulphuric acid*, forming compound acids of the form $C^nH^{2n}.SH^2O^4$, or $\left.\begin{matrix}(SO^2)'' \\ C^nH^{2n+1} \\ H\end{matrix}\right\}O^2$, homologous with ethyl-sulphuric or sulphovinic acid. This reaction is of especial importance, since it enables us to pass from an olefine to the corresponding alcohol: thus ethylene-gas shaken up with strong sulphuric acid yields ethyl-sulphuric acid, $\left.\begin{matrix}SO^2 \\ C^2H^5.H\end{matrix}\right\}O^2$, whence, by distillation with water, ethylic alcohol is obtained (i. 72).

Olefines also combine with *water*, *hydrochloric acid*, *hydrobromic acid*, &c. Wurtz has shown (Ann. Ch. Pharm. cxxv. 114) that amylene combines with hydrobromic and hydriodic acid, forming compounds isomeric with iodide and bromide of amyl; and by treating the hydriodate, $C^5H^{10}.HI$, with moist oxide of silver, he has obtained a hydrate of amylene, $C^5H^{10}.H^2O$, isomeric with amylic alcohol. All these compounds are distinguished from the amyl-compounds, with which they are isomeric, by the facility with which they give up their amylene under the influence of various reagents. Thus hydrate of amylene quickly absorbs hydriodic acid gas, and is resolved into hydriodate of amylene and aqueous hydriodic acid; similarly with hydrochloric acid. Bromine also decomposes it rapidly into bromide of amylene and water; chlorine similarly but less quickly. With sodium it yields the compound $C^5H^{10}.NaHO$, which when treated with hydriodate of amylene, readily yields amylene, hydrate of amylene, and iodide of sodium:

$$C^5H^{10}.NaHO + C^5H^{10}.HI = C^5H^{10} + C^5H^{10}.H^2O + NaI.$$

Hydriodate of amylene is also rapidly decomposed by sodium, yielding iodide of sodium, amylene, and free hydrogen. With alcoholic potash, it yields amylene and iodide of potassium; with ammonia, the products are iodide of ammonium, amylene, and a small quantity of a base isomeric or perhaps identical with amylamine.

The amylene in all these compounds appears to be but loosely united with the water or the acid, and is set at liberty on the slightest disturbance; whereas in their isomers the amyl-compounds, the group C^5H^{11}, which is not capable of existing in the separate state, is easily transferred from one compound to another, and it is only with considerable difficulty that two molecules of it can be made to coalesce into one so as to form free amyl, $C^{10}H^{22}$.

Hexylene, C^6H^{12}, also unites with hydriodic acid, and the hydriodate, treated with water and oxide of silver, yields a hydrate, $C^6H^{12}.H^2O$, isomeric with hexylic alcohol, and possibly identical with the β hexylic alcohol discovered by Wanklyn and Erlenmeyer.

The formation and properties of the alcohol-radicles (i. 96) and their hydrides (iii. 180) have already been considered. Recent investigations seem to show that there is no essential difference between the alcohol-radicles in the free state, and their hydrides (pp. 144, 182).

Of the hydrocarbons, C^nH^{2n-2}, homologous with acetylene, only three have been obtained, viz. acetylene, C^2H^2 (i. 1111), allylene, C^3H^4 (i. 1112), and crotonylene, C^4H^6 (ii. 965).

Of the hydrocarbons, C^nH^{2n-6}, homologous with benzene, five are known, viz. benzene, C^6H^6 (i. 541), benzylene or toluene, C^7H^8 (i. 577), xylene, C^8H^{10}, cumene, C^9H^{12} (ii. 173), and cymene, $C^{10}H^{14}$ (ii. 296). They have all been specially considered, excepting xylene, which will be described in its place. These hydrocarbons, as already observed, are produced by the destructive distillation of coal and other organic substances at high temperatures; also in a great variety of chemical reactions (see BENZENE). They are distinguished by the facility with which they form substitution-compounds with concentrated nitric acid, *e.g.* nitrobenzene, $C^6H^5(NO^2)$. These nitro-compounds, being heavy oily liquids of rather high boiling point, afford the means of separating these hydrocarbons from others, such as the alcoholic hydrides, with which they may be mixed (p. 146). The same compounds subjected to the action of reducing agents, such as sulphydric acid or ferrous acetate, yield organic bases, which may be supposed to be derived from the nitro-compound by substitution of amidogen, NH^2, for nitryl, NO^2, *e.g.* aniline, $C^6H^5(H^2N)$, from nitrobenzene.

The camphenes, or terebenes, $C^{10}H^{16}$, isomeric with oil of turpentine, exist ready formed in a great number of plants. For their general properties see vol. i. p. 724.

The hydrocarbons are the simplest of all organic compounds, and may be regarded as the starting-points from which all others may be derived, by substitution or addition (see NUCLEUS-THEORY and RADICLES). Hence, of late years, the attention of chemists has been very much directed to the discovery of methods for producing these compounds directly from their inorganic elements; since, when this is accomplished, the formation of a great number of the more complex organic compounds, by the synthesis of their elements, becomes a comparatively easy matter The most successful efforts in this direction have been made by Berthelot (Chem. Soc. J. xvii. 37), who has succeeded in producing certain hydrocarbons by direct combination of the elements carbon and hydrogen, and from these producing others of great complexity.

1. Acetylene, C^2H^2, is produced when hydrogen is passed over carbon heated to bright redness by the electric arc. This gas, passed into a solution of cuprous chloride, forms cuprous acetylene, C^2CcuH; and this compound, subjected to the action of nascent hydrogen (evolved by the action of zinc on ammonia), yields ethylene:

$$\underset{\text{Acetylene.}}{C^2H^2} + H^2 = \underset{\text{Ethylene.}}{C^2H^4}$$

Ethylene thus obtained may be converted into alcohol, and from this a host of other compounds, ethers, acetones, acids, amines, &c. may be derived.

2. Hydrocarbons may be formed from inorganic compounds containing their elements, such as water and sulphide of carbon, or carbonic anhydride. A mixture of sulphydric acid and sulphide of carbon, subjected to the action of copper at a red-heat, yields marsh-gas:

$$CS^2 + 2H^2S + 8Cu = CH^4 + 4Cu^2S.$$

Marsh-gas may also be formed from carbonic anhydride, though by a less direct process, viz. by first converting the latter compound into carbonic oxide, this into formic acid ($CO + H^2O = CH^2O^2$, ii. 683), then subjecting a salt of this acid, the barium-salt, for example, to dry distillation:

$$4CHBaO^2 = CH^4 + CO^2 + 2Ba^2CO^3.$$

Marsh-gas, mixed with an equal volume of chlorine, yields chloride of methyl, CH^3Cl; and this ether distilled with potash, yields methylic alcohol, CH^4O, which is formed by the addition of 1 at. oxygen to marsh gas, whereas ethylic alcohol is formed from ethylene by the addition of the elements of water. These two modes of formation of alcohols from hydrocarbons are general, the former applying to all homologues of marsh-gas, the latter to all homologues of ethylene.

3. A hydrocarbon may be transformed into another of greater complexity: *a.* By *direct condensation.* Marsh-gas raised to a very high temperature, or subjected to the action of a series of induction-sparks, is converted into acetylene, which contains twice the quantity of carbon in the same volume: $2CH^4 = C^2H^2 + H^2$. The condensation of marsh gas may, however, be carried considerably further, and made to yield naphthalene, a hydrocarbon containing ten times as much carbon in the same volume: $10CH^4 = C^{10}H^8 + H^{32}$ viz. by enclosing the marsh-gas in a tube of very refractory glass, and keeping it for several hours at a temperature as near as possible to that at which Bohemian glass softens. The condensation may also be effected by subjecting the vapour of bromoform, $CHBr^3$ (tribrominated methylic hydride), to the action of copper at a red heat, so as to remove the bromine. The residue, CH, then suffers a six-fold condensation, yielding benzene, C^6H^6.

b. By the union of two simple molecules into a more complex molecule. Thus, when a mixture of marsh-gas and carbonic oxide is slowly passed through a tube heated to low redness, tritylene, C^3H^6, is produced:

$$2CH^4 + CO = C^3H^6 + H^2O.$$

This reaction may perhaps explain the formation of a small quantity of tritylene in the distillation of formate of barium; and it is doubtless to reactions of the same order that we may attribute the production of hydrocarbons of the same series, which has been experimentally demonstrated as high as amylene, in the distillation of acetates.

There are also other ways in which complex hydrocarbons may be built up by the union of those of more simple constitution. Wurtz has shown (Ann. Ch. Pharm. cxxiii. 202; cxxvii. 55), that amylene, C^5H^{10}, may be produced by the union of the alcohol-radicles ethyl and allyl:

$$C^2H^5 + C^3H^5 = C^5H^{10},$$

this combination being brought about by the mutual action of zinc-ethyl and iodide of allyl. A number of other hydrocarbons are, however, formed at the same time, the following having been isolated and analysed:

C^2H^4	C^3H^6	C^5H^{10}	C^5H^{12}	C^6H^{10}	$C^{10}H^{20}$
Ethylene.	Tritylene.	Amylene.	Hydride of amyl.	Allyl.	Decatylene.

The ethylene and tritylene are produced by the mutual action of the ethyl and allyl groups:

$$C^2H^5 + C^3H^5 = C^2H^4 + C^3H^6.$$

Decatylene, $C^{10}H^{20}$, results from the condensation of two molecules of amylene into one. Besides these compounds, there are also formed other hydrocarbons, boiling above 200° (decatylene, the least volatile of those above-mentioned, boils at 160°), and containing, like allyl, a smaller proportion of hydrogen than the olefines. The formation of these hydrocarbons explains that of hydride of amyl, in which the proportion of hydrogen is larger than in the olefines.

The hydrocarbon, C^5H^{10}, obtained in the reaction just described, possesses the principal physical and chemical properties of amylene produced from amylic alcohol by the action of chloride of zinc, and, therefore, is not merely an isomer (ethyl-allyl) of that compound. This formation of amylene from two hydrocarbons of lower molecular weight is analogous to that of chloride of heptyl, $C^7H^{15}Cl$, by the action of chlorine on ethyl-amyl, $C^2H^5.C^5H^{11}$, and of chloride of decatyl, $C^{10}H^{21}Cl$, by that of chlorine on amyl itself, observed by Schorlemmer.

HYDROCARBOXYLIC ACIDS. (Lerch, Ann. Ch. Pharm. cxxiv. 20; Rép. Chim. pure, 1863, p. 143; Jahresb. 1862, p. 276.)—This name is applied to three acids produced, together with others, by the decomposition of carboxide of potassium, the black amorphous substance formed in the preparation of potassium in the ordinary way, and likewise by the direct combination of potassium with carbonic oxide. This substance remains unaltered when kept in rock-oil or in a dry vacuum, but when exposed to the air, it absorbs moisture rapidly, acquiring a cherry-red and finally a yellow colour: it absorbs oxygen only when moist. When treated with water, alcohol or ether, out of contact with the air, it gives off gas, and leaves a black glutinous substance, which turns red on exposure to the air, and dissolves in water with red colour and without disengagement of gas. This mass yields, besides oxalic acid, three series of acids, including croconic acid (ii. 109).

Perfectly unaltered carboxide of potassium, to which Brodie assigns the formula $C^nH^nK^n$, yields, when treated with hydrochloric acid, an acid crystallising in white needles and having the composition $C^{10}H^{10}O^{10}$; this is trihydrocarboxylic acid.

If the carboxide of potassium be first treated with alcohol and then with hydrochloric acid, it yields black needles of dihydrocarboxylic acid, $C^5H^4O^5$ or $C^{10}H^8O^{10}$

If the air has had access to the mass before or after the treatment with alcohol, it afterwards yields, with hydrochloric acid, dark garnet-red crystals of hydrocarboxylic acid, $C^{10}H^6O^{10}$.

Lastly, if the mass has been left in contact with the air till it has turned quite red, and it is then treated with hydrochloric acid, a fourth acid is obtained, called carboxylic acid, the potassium-salts of which are composed according to the formulæ $C^{10}HK^3O^{10}$ and $C^{10}K^4O^{10}$. On attempting to isolate this acid, fine colourless prisms of rhodizonic acid, $C^5H^4O^6$, are obtained, being derived from the preceding by fixation of water, and splitting up of the molecule:

$$C^{10}H^4O^{10} + 2H^2O = 2C^5H^4O^6.$$

In addition to these acids, croconic acid, $C^5H^2O^5$ (formed from carboxylic acid by division of the molecule), and oxalic acid, are obtained as final products of the oxidation.

The formation of dihydrocarboxylic, hydrocarboxylic, and carboxylic acids by oxidation of trihydrocarboxylic acid is represented by the following equations:

$$\begin{array}{lcclcl} C^{10}H^{10}O^{10} & + & O & = & C^{10}H^8O^{10} & + & H^2O. \\ C^{10}H^8O^{10} & + & O & = & C^{10}H^6O^{10} & + & H^2O. \\ C^{10}H^6O^{10} & + & O & = & C^{10}H^4O^{10} & + & H^2O. \end{array}$$

Trihydrocarboxylic acid. $C^{10}H^{10}O^{10} = \left.\begin{matrix} C^{10}H^6O^6 \\ H^4 \end{matrix}\right\} O^4$.—This acid is produced, as already observed, by the action of hydrochloric acid on carboxide of potassium which has not been exposed to the air; also by the reduction of dihydrocarboxylic acid. It forms white silky needles which, when exposed to moist air, quickly turn red, and are ultimately converted into dihydrocarboxylic acid. Its solution is acid, colourless, and very sensitive to the action of oxidising agents. By nitrate of potassium, it is converted into oxycarboxylic acid, with evolution of nitrogen. Of the 10 at. hydrogen contained in its molecule, 6 at. are easily removed by oxidation, giving rise to new radicles, viz. those of dihydrocarboxylic, hydrocarboxylic and carboxylic acids, whereas the remaining 4 at. are basic, and easily replaceable by metals, but not removable by oxidation. In the potassium-salt also, $C^{10}K^{10}O^{10}$, 6 at. K may be removed, two at a time, by oxidation, whereas the remaining 4 at. K appear to be irremovable: hence the rational formula of the acid above given. In like manner, dihydrocarboxylic acid contains 4 at., and hydrocarboxylic acid, 2 at. H, removable by oxidation.

The trihydrocarboxylates of the alkali-metals are soluble in water, the other salts are sparingly soluble or insoluble: they all become coloured by exposure to the air, yielding salts of the following acids:

Dihydrocarboxylic acid. $C^{10}H^8O^{10} = \left.\begin{matrix} C^{10}H^4O^6 \\ H^4 \end{matrix}\right\} O^4$.—This acid forms black metallic-shining monoclinic crystals, grouped in very thin tufts; the thinner crystals have a wood-yellow colour, and exhibit trichroïsm. They are permanent in the air, even at 100°, dissolve readily in water and alcohol, slowly in ether; the solutions are red by transmitted, violet by reflected light.

The salts of this acid are as unstable as those of the preceding. Those of the alkali-metals are black, soluble in water and crystallisable; the rest are blue or red precipitates; they are very easily converted by oxidation into rhodizonates or carboxylates.

Hydrocarboxylic acid, $C^{10}H^6O^{10} = \left.\begin{matrix} C^{10}H^2O^6 \\ H^4 \end{matrix}\right\} O^4$, was obtained accidentally in the preparation of the preceding acid from a black mass which had undergone partial alteration. It crystallises from alcohol in long brown needles, which in contact with water are immediately resolved into dihydrocarboxylic and rhodizonic acids:

$$2C^{10}H^6O^{10} + 2H^2O = C^{10}H^8O^{10} + 2C^5H^4O^6.$$

HYDROCAROTIN. $C^{18}H^{30}O$. (Husemann, Ann. Ch. Pharm. cxvii. 200; Jahresber. 1861, p. 754).—A substance contained, together with carotin (i. 805), in the root of the carrot (*Daucus carota*). To obtain these substances, the crushed carrots are pressed, the residue is repeatedly washed out with water, and the united solutions are mixed with a little dilute sulphuric acid and tincture of galls (which facilitates the separation of the coagulum); the glutinous precipitate, freed by pressure from the enclosed liquid, is boiled six or seven times in the half-dry state with 5 or 6 vol. of alcohol of 80 per cent.; and the residue is treated with sulphide of carbon to extract the carotin. The alcoholic extract contains hydrocarotin together with mannite (if the carrots are a year old, but not if they are fresh), sugar, a fixed oil, and a small portion of carotin.

Hydrocarotin crystallises from the alcoholic extract, after long standing, in laminar crystals, which may be freed from mannite (if present) by recrystallisation from hot alcohol, and finally by boiling with water. It is tasteless and inodorous, crystallises in large colourless silky laminæ, from ether in flat rhombic prisms; is lighter than water (which does not wet it); melts at 126·8°; dissolves in alcohol, and more easily in ether, sulphide of carbon, benzene, volatile oils, and chloroform. When heated above 100°, it turns yellow to yellowish red; after fusion it remains amorphous, and then dissolves less easily in benzene and sulphide of carbon.

Hydrocarotin is not precipitated from its alcoholic solution by metallic salts or tannic acid; it is not altered by the action of caustic alkalis, strong acids, or oxidising agents: with *fuming nitric acid*, it appears to form a nitro-compound. Strong *sulphuric acid* colours it red and dissolves it completely at a gentle heat, forming a solution from which it is precipitated by water apparently unaltered, but in the amorphous state. With *chlorine* it forms a resinous substitution-product, $C^{18}H^{26}Cl^4O$; with *bromine* a similar body, $C^{18}H^{27}Br^3O$, whose ethereal solution, when treated with alcoholic potash, gives up bromine, and forms a yellowish-red substance soluble with blood-red colour in sulphide of carbon. *Iodine* also, in sunshine, appears to form a substitution-product with hydrocarotin.

HYDROCERITE. See LANTHANITE.

HYDROCHINONE. See HYDROQUINONE.

HYDROCHLORE. See PYROCHLORE.

HYDROCHLORIC ACID. See CHLORHYDRIC ACID (i. 890).

HYDROCHRYSAMIDE. $C^7H^6N^2O^3$. (Schunck, Ann. Ch. Pharm. lxv. 231.) —A compound produced by the action of reducing agents on chrysammic acid (i. 955). It may be prepared by adding chrysammic acid to a boiling solution of sulphide of potassium containing excess of caustic potash; or to a boiling solution of protochloride of tin, afterwards removing the excess of acid, dissolving the residue in boiling potash, and leaving the solution to crystallise. It is difficult, however, by the latter method to obtain it free from oxide of tin.

Hydrochrysamide forms needle-shaped crystals, of a fine blue colour by transmitted, and metallic red by reflected light. Heated in a small tube, it gives off violet vapours, which condense in crystals on the cold parts of the tube; the greater part, however, is decomposed, giving off ammonia and leaving charcoal. It is insoluble in boiling *water*, and sparingly soluble in boiling *alcohol*, to which it imparts a faint blue tint. It is dissolved by strong *sulphuric acid*, and reprecipitated in blue flakes by water.— It is decomposed by boiling *nitric acid*, and by *chlorine* in presence of water. It dissolves in *potash* and in *alkaline carbonates*, forming solutions of the colour of sulphindigotic acid; acids precipitate it therefrom in blue flakes.

HYDROCINNAMIDE. $C^{27}H^{24}N^2 = N^2(\overset{\prime\prime}{C^9H^8})^3$. *Cinnhydramide. Hydride of Azocinnamyl.* (Laurent, Rev. scient. x. 119.)—Produced by the action of ammonia on hydride of cinnamyl:

$$3C^9H^8O \ + \ 2NH^3 \ = \ N^2(C^9H^8)^3 \ + \ 3H^2O.$$

When purified by recrystallisation from hot alcohol and ether, it forms colourless right prisms with rectangular base, but having their bases replaced by two triangular facets, meeting at a very obtuse angle. It is inodorous, insoluble in water, fusible, and solidifies on cooling to a transparent amorphous mass like gum. It is decomposed by distillation, yielding an oil and a solid substance. It is not decomposed by boiling hydrochloric acid, or by alcoholic potash; but boiling nitric acid decomposes it, yielding a product which melts in boiling water.

Dumas and Peligot, by treating oil of cinnamon with dry ammonia gas, obtained a product which crystallised from alcohol and ether in silky tufts, and to which they assigned the formula $C^9H^8O.NH^3$, but it probably consisted mainly of hydrocinnamide. (*Gerhardt's Traité*, iii. 385.)

HYDROCOTYLE ASIATICA. A plant used in India as a remedy against various cutaneous diseases. According to Lepire (J. Pharm. [3] xxviii. 47), it contains a peculiar principle, *vellarin* (from the Tamul name of the plant, *vallârai*), which he describes as a bitter, strong-smelling oil, soluble in weak alcohol and in ether, thickening on exposure to the air, soluble in aqueous ammonia, insoluble in potash.

HYDROCROCONIC ACID. $C^5H^4O^5 = \left.\begin{matrix}C^5H^2O^3\\H^2\end{matrix}\right\}O^2$. (Lerch, Ann. Ch. Pharm. cxxiv. 20.)—An acid produced by the action of hydriodic acid on croconate of potassium in closed vessels. On mixing the product of the reaction with alcoholic potash-solution, hydrocroconate of potassium, $C^5H^2K^2O^5$, separates as a dingy red precipitate, which crystallises from hot water in crimson needles. The blood-red solution of this salt is converted into croconate (and a small quantity of oxalate) of potassium on exposure to the air, expecially in presence of alkali.

Hydrocroconic acid is soluble in water, alcohol, and ether, and does not crystallise. The *barium-salt*, $C^5H^2Ba^2O^5$, is a pæony-red precipitate, soluble in hydrochloric, insoluble in acetic acid. The *lead-salt*, $C^5H^2Pb^2O^5$, is also a red precipitate.

HYDROCYANHARMALINE. See HARMALINE (p. 8).

HYDROCYANIC ACID. See CYANIDE OF HYDROGEN (ii. 214).

HYDRODOLOMITE. A hydromagnesite, having part of the magnesium replaced by calcium. Occurs on Somma in isolated sinter-like, globular or stalactitic, earthy masses, having a white or yellowish white colour. According to Kobell (J. pr. Chem. xxxvi. 304), it contains 25·22 per cent. lime, 24·28 magnesia, 33·10 carbonic anhydride, and 17·40 water: whence the formula $3[(Mg^2; Ca^2)CO^2.H^2O] + 2MgHO$. (Rammelsberg.)

HYDRO-ELECTRIC MACHINE. See ELECTRICITY (ii. 408).

HYDROFERRICYANIC ACID. See FERRICYANIDES (ii. 244).

HYDROFERROCYANIC ACID. See FERROCYANIDES (ii. 226).

HYDROFLUOBORATES. See BORON, FLUORIDE OF (i. 632).

HYDROFLUOSILICATES. See SILICON, FLUORIDE OF.

HYDROGALACTOMETER. An arrangement described by Zenneck (Jahrb. pr. Pharm. xx. 65; Jahresb. 1850, p. 619) for determining the amount of water added to normal milk. The milk is coagulated by a few drops of hydrochloric acid, and the volume of the curd, separated by filtration through flannel, is compared with that obtained in a similar manner from pure milk.

HYDROGEN. *Atomic weight* = 1. *Symbol* H. (*Inflammable air, Wasserstoff, Hydrogenium.*)—The older alchemists do not appear to have been acquainted with this gas. The evolution of an air during the solution of iron in sulphuric acid was first noticed in the sixteenth century by Paracelsus. The inflammability of the air thus produced, was observed in the seventeenth century by Turquet de Mayerne, and afterwards (1672) by Boyle, in his "New Experiments touching the relation between Flame and Air." Lemery in 1700 observed the detonating property of this inflammable gas. But the first exact experiments on its nature were made in 1766 by Cavendish, who showed that it is a peculiar kind of air, which he called *inflammable air;* that it is produced when iron, zinc, or tin is dissolved in dilute sulphuric or hydrochloric acid; and that different metals evolve different quantities of the gas. He also estimated its specific gravity at $\frac{1}{11}$ of that of common air. (It is really about $\frac{1}{14}$.)

The inflammable air generated in these processes was, however, for some time confounded with other kinds of inflammable air, such as those produced by the destructive distillation of organic bodies, by the imperfect combustion of charcoal—with vapour of ether, &c., all of which were supposed to consist essentially of the same inflammable principle modified by the admixture of other substances. Moreover, it was supposed that the inflammable principle developed in the solution of metals in acids, proceeded from the metal, and that it was either phlogiston or intimately related thereto.

The production of moisture in the burning of hydrogen, appears to have been first noticed by Macquer and De la Methérie, in 1766; but no one at that time supposed that the only product of the combustion was water. Lavoisier supposed that hydrogen, like other combustible bodies, produced an acid in burning, and made several unsuccessful experiments to obtain this acid. But the grand discovery that water is the sole product of the combustion of hydrogen was made by Cavendish, in 1781, and published in 1783. Cavendish showed that 423 volumes of hydrogen required for combustion 1,000 volumes of air (which contain 210 volumes of oxygen, and will, therefore, burn exactly 420 volumes of hydrogen); and, moreover, that when hydrogen and oxygen gases are burnt together in certain proportions, nearly all the gas disappears, nothing but slight impurities remaining behind. These results were afterwards fully confirmed by the experiments of Lavoisier and Laplace (see GAS, ii. 780).

Sources.—Hydrogen is never found in the free state. The compound which contains it in the greatest abundance is marsh-gas, of which it forms one-fourth. Of water it forms one-ninth. It occurs in smaller quantities in combination with phosphorus, sulphur, iodine, bromine, carbon and nitrogen, and is an essential constituent of nearly all organic compounds.

Preparation.—Hydrogen is generally obtained by the decomposition of water, or of dilute acids.—1. It is produced in the state of greatest purity by electrolysis, as already explained in the article ANALYSIS OF GASES (i. 285).

2. By passing vapour of water over iron nails or wire contained in a gun-barrel, laid horizontally in a furnace, and heated to bright redness. The iron is thereby converted

into ferroso-ferric oxide, Fe^3O^4, while hydrogen gas passes over, and may be collected over water.

3. By introducing potassium or sodium into an inverted tube or cylinder filled with water or alcohol, and standing in a vessel of the same liquid. It is best to wrap the metal in a piece of paper before plunging it under the mouth of the cylinder:

$$H^2O + Na = \underset{\text{Hydrate of sodium.}}{NaHO} + H.$$

$$\underset{\text{Alcohol.}}{C^2H^6O} + Na = \underset{\text{Ethylate of sodium.}}{C^2H^5NaO} + H.$$

4. By dissolving zinc or iron in sulphuric acid diluted with an eight-fold quantity of water, or in hydrochloric acid diluted with twice its weight of water:

$$H^2SO^4 + Zn^2 = Zn^2SO^4 + H^2,$$

and

$$HCl + Zn = ZnCl + H.$$

This is the most convenient method of obtaining the gas for general purposes.—5. By dissolving zinc, in contact with iron or platinum, in solution of caustic potash, zincate of potassium being then formed:

$$\underset{\text{Hydrate of potassium.}}{KHO} + Zn = \underset{\text{Zincate of potassium.}}{ZnKO} + H.$$

The use of the iron is to form an electric couple with the zinc, the latter then acting on the positive or active metal.

6. By acting on cuprous hydride with hydrochloric acid:

$$Cu^2H + HCl = Cu^2Cl + H^2.$$

7. By heating formates or oxalates with excess of hydrate of potassium, sodium, or calcium:

$$\underset{\text{Formate of potassium.}}{CHKO^2} + KHO = \underset{\text{Carbonate of potassium.}}{CK^2O^3} + H^2.$$

$$\underset{\text{Oxalate of potassium.}}{C^2K^2O^4} + 2KHO = 2CK^2O^3 + H^2.$$

8. By the action of hydrate of potassium on certain organic bodies having a tendency to form acids by oxidation:

$$\underset{\text{Hydride of benzoyl.}}{C^7H^6O} + KHO = \underset{\text{Benzoate of potassium.}}{C^7H^5KO^2} + H^2.$$

Purification.—Hydrogen prepared by dissolving zinc or iron in sulphuric acid—which is the method most used—may contain the following impurities:—1. *Sulphurous acid*, if this acid is present in the sulphuric acid used.—2. *Nitrous oxide* or *nitric oxide gas*, if the sulphuric acid contains nitric oxide, nitrous acid, or nitric acid.—3. *Sulphydric acid*, if the zinc contains sulphide of zinc, or if the sulphuric acid contains sulphurous acid—or if a fresh quantity of strong sulphuric acid be added to the dilute acid already acting on the zinc, without mixing it well with the liquid.—4. *Phosphoretted hydrogen*, if the zinc contains phosphorus.—5. *Arsenetted hydrogen*, if the zinc contains arsenic, or if the sulphuric acid contains arsenious acid.—6. *Carbonic anhydride* has occasionally been observed in hydrogen prepared with peculiar kinds of zinc. These impurities, which give the gas an unpleasant odour, may be removed by passing it over substances which absorb or decompose the adventitious gases. Dumas passed the gas through two U-tubes, each about three feet long, and filled with broken glass, the glass in the first tube being moistened with nitrate of lead, which removes the sulphydric acid, and that in the second with sulphate of silver, by which the arsenetted hydrogen is separated; then through a third U-tube filled with fragments of pumice-stone saturated with strong potash; and, lastly, to render it anhydrous, first through a tube containing fragments of hydrate of potassium, then through another containing phosphoric anhydride or pumice-stone soaked in oil of vitriol. To avoid the presence of oxides of nitrogen, it is best to use sulphuric acid perfectly free from those oxides.

Hydrogen gas obtained by the use of iron may contain the same impurities as that prepared with zinc—and in addition:—1. *Ferruretted hydrogen*—to be removed by fuming nitric acid or solution of mercuric chloride; and 2. The vapour of an oily hydrocarbon, which is produced in larger quantity as the iron contains more carbon, and communicates a peculiarly repulsive odour to the gas. It may be removed by passing the gas through alcohol, and the alcohol may be afterwards separated by water.

According to Döbereiner (Schw. J. iii. 377), the gas obtained with either zinc or iron may be deprived of all odour by 24 hours' contact with moistened charcoal powder.

In whatever manner the gas may be prepared, it generally contains a small quantity of atmospheric air, proceeding from the liquids used in the preparation. The nitrogen cannot be removed; but the oxygen may be separated by leaving the gas for a while in contact with spongy platinum, which causes the oxygen to unite with a portion of the hydrogen and form water.

Properties.—Hydrogen is a colourless gas, of specific gravity 0·0693. It is the lightest of all known substances, being about 14½ times as light as atmospheric air; it may therefore be used for inflating balloons. Soap-bubbles filled with it rise rapidly in the air. It escapes rapidly out of vessels with their mouths turned upwards; but a wide-mouthed vessel filled with it may be carried with its mouth downwards for a considerable distance without the gas escaping. For the same reason, it is easily collected by displacement, without the use of water, viz. by holding the vessel which is to receive it, over the extremity of a vertical tube attached to the mouth of the generating vessel.

Hydrogen is odourless when quite pure, but as usually prepared, it has a disagreeable odour, arising from impurities. Small animals introduced into the gas die instantly. In man, the pure gas excites, after two inspirations, disagreeable sensations and loss of muscular power; when mixed with air, it may be breathed for a longer time, but imparts a peculiar squeaking tone to the voice. It is not directly injurious, but so long as it is inhaled, oxygen gas, which is essential to life, is prevented from entering the lungs.

Hydrogen is very inflammable, and burns in the air with a pale blue flame. It does not support the combustion of those bodies which burn in the air: for instance, if a jar full of hydrogen be held with its mouth downwards, and a lighted taper plunged into it, the hydrogen will be set on fire at the mouth, but the taper will be extinguished. A jet of oxygen will, however, burn in hydrogen, as well as a jet of hydrogen in oxygen, though with a somewhat different appearance. The experiment may be made by setting fire to hydrogen-gas at the mouth of a bottle, and then directing a jet of oxygen through the flame into the body of the gas. A flame will then be formed at the orifice of the jet, and will continue to burn till the hydrogen is exhausted.

Hydrogen and *oxygen* unite to form water, in the proportion of 2 volumes of hydrogen to 1 volume of oxygen; and when the gases are mixed in these proportions, they may be made to unite, either slowly or rapidly, the entire volume of gas disappearing. On bringing a burning body in contact with the mixture, or passing an electric spark through it, combination instantly takes place throughout the whole mass, attended with great and sudden rise of temperature, whereby the mixed gases, or rather the watery vapour resulting from their union, are expended with a force sufficient to shatter the containing vessel, if not of great strength. If the vessel is entirely closed, and strong enough to resist the expansive force of the gas, no noise is heard; but if the mouth of the vessel be left open, or the gas be able to force for itself a passage into the air, a loud detonation is the result, arising from the concussion of the air by the escaping gases. The same effect is produced, though with much less intensity, when a mixture of 2 vol. hydrogen and 5 vol. atmospheric air (containing 1 vol. oxygen, the quantity required to unite with 2 vol. hydrogen) is exposed to the action of flame or the electric spark. Hence, in manipulating with hydrogen, great care must be taken to prevent accidental admixture of air, as, if such admixture takes place unknown to the operator, explosions of dangerous character may ensue when the gas comes in contact with flame. In collecting the gas, a considerable quantity should be suffered to escape before any of it is collected, so that the air in the apparatus may be completely eliminated.

The rapid combination of hydrogen and oxygen may be brought about, not only by the contact of flame, but also by the heat of a red-hot iron wire, or a coal hot enough to exhibit a visible glow by daylight. According to Biot (Gilb. Ann. xx. 99), the heat produced by suddenly compressing the detonating gas, is sufficient to cause the explosion.

The presence of certain metals causes the gases to unite, even at ordinary temperatures. This effect is exhibited most strikingly by platinum, in the form of platinum-sponge or platinum-black (see PLATINUM); but it is also produced by a plate of the metal rendered perfectly clean by rubbing it while hot with fused potash, then washing it with water, dipping it into hot oil of vitriol, and again washing with water. Similar effects are exhibited, though with less facility, by spongy iridium and osmium, finely divided palladium, gold in the form of leaves or dust, and silver leaf. This peculiar action of platinum and other metals appears to be due (in part at least) to the absorption of the gases by the metal, and their condensation within its pores. (See GASES, ABSORPTION OF, BY SOLIDS, ii. 804.)

The flame of hydrogen, though but feebly luminous, is intensely hot, and when a jet of oxygen is directed through it, as in the oxy-hydrogen blowpipe, the proportions of the two gases being properly adjusted so that neither of them is in excess, the heat produced is the highest that can be obtained by chemical combination. (See BLOW-PIPE, OXY-HYDROGEN, i. 616.)

Hydrogen likewise unites very energetically with *chlorine*, forming hydrochloric acid. The gases, in equal volumes, may be mixed in the dark without uniting, but on exposure to diffused daylight, combination takes place gradually, and exposure to the direct rays of the sun, or to the light of the electric arc, or of lime ignited by the oxy-hydrogen flame, causes instant combination, attended with violent explosion. Explosion is also produced by contact with flame, or with a brick heated to 150° C. With *bromine-vapour*, hydrogen does not unite at ordinary temperatures, even in sunshine; but partial combination is effected by contact with a red-hot wire. With *iodine*, it unites when a mixture of hydrogen and iodine-vapour is passed through a red-hot tube, and, according to Blundell (Pogg. Ann. ii. 216), at ordinary temperatures under the influence of spongy platinum. With other elements hydrogen does not unite directly.

Hydrogen is an essential constituent of acids—properly so called—these bodies being in fact salts of hydrogen. (See ACIDS, i. 39.) It also forms basic compounds, viz. ammonia, arsenetted, antimonetted hydrogen, &c.; and unites with metals and organic radicles, forming compounds called hydrides (p. 180).

HYDROGEN, ANTIMONIDE OF. See ANTIMONY, HYDRIDE OF (i. 322).

HYDROGEN, ARSENIDES OF. See ARSENIC, HYDRIDES OF (i. 371).

HYDROGEN, BROMIDE OF. See BROMIDE OF HYDROGEN (i. 672).

HYDROGEN, CHLORIDE OF. See CHLORHYDRIC ACID (i. 890).

HYDROGEN, FLUORIDE OF. See FLUORHYDRIC ACID (ii. 669).

HYDROGEN, IODIDE OF. See IODHYDRIC ACID.

HYDROGEN, OXIDES OF. Hydrogen forms two, or perhaps three, compounds with oxygen, viz. the *Protoxide* or water, H^2O; the *dioxide* or *peroxide*, $H\,O^2$, and perhaps *Ozone*, which according to Baumert is a *trioxide* of hydrogen, H^2O^3.

Water. H^2O.—The properties of water will be described in a separate article; we shall here speak only of its composition. We have already stated that when pure oxygen and pure hydrogen are mixed in the proportion of 2 vol. H to 1 vol. O, and exploded, the entire volume of gas disappears and nothing is produced but water. Now the density of oxygen is 16 times as great as that of hydrogen: hence water is composed, by weight, of 8 pts. of oxygen to 1 pt. of hydrogen. This composition has hitherto been most generally represented by the formula *HO*, water being thus regarded as a compound of hydrogen and oxygen in equal numbers of atoms, and the atom of oxygen being supposed to weigh 8 times as much as that of hydrogen. But there are many reasons for supposing that a molecule of water contains 2 at. of hydrogen united with 1 at. of oxygen—a composition represented by the formula $\begin{matrix}H\\H\end{matrix}O$ or H^2O. These reasons have already been given in the article ATOMIC WEIGHTS (i. 461), and need not here be repeated. We will merely mention that, according to the formula H^2O, the atomic weights of oxygen and hydrogen are to one another as the densities of the two gases, which is the most simple supposition that can be made respecting them, and is in accordance with the conclusions deduced from the dynamical theory of heat (p. 132).

The composition of water by weight and volume may be ascertained in various other ways, besides the direct combination of the component gases. When water is decomposed by electrolysis, the gases are evolved very nearly in the proportion of 2 vol. H to 1 vol. O, but the volume of oxygen is always somewhat less than it should be on account of its greater absorbability in water. The composition might also be ascertained by passing vapour of water over red-hot iron, measuring the volume of the hydrogen evolved, and determining the increase in weight of the iron.

But the most exact method is that adopted by Berzelius and Dulong (Ann. Ch. Phys. [2] xv. 86) and by Dumas (Ann. Ch. Phys. [3] viii. 189), which consists in passing pure and dry hydrogen gas, obtained as described at p. 193, over red-hot oxide of copper. This oxide then gives up its oxygen to the hydrogen, and forms water, which is collected, partly in a small receiver attached to the end of the tube containing the oxide of copper, partly in a tube containing dry chloride of calcium. The quantity of water thus produced is weighed, and the loss of weight which the oxide of copper sustains by parting with its oxygen, is likewise determined. These experiments show that water is composed exactly in the proportion of 8 pts. by weight of oxygen to 1 pt. of hydrogen:

Calculation.			Dumas.	Berzelius and Dulong.
H^2	2	11·11	11·11	11·1
O	16	88·89	88·89	88·9
H^2O	18	100·00	100·00	100·0

For the compounds of water, see HYDRATES (p. 179).

Dioxide, or Peroxide of Hydrogen. HO or H^2O^2.—This remarkable compound was discovered by Thénard (*Traité de Chimie*, 4$^{\text{me}}$. éd. iv. 2, 41).—It is produced when peroxide of potassium, sodium, barium, strontium, or calcium is digested in any acid which forms a soluble salt with the base resulting from the decomposition of the peroxide, the excess of oxygen not escaping as gas, but passing over to a portion of the water, and converting it into peroxide of hydrogen, *e.g.*:

$$BaO + HCl = 2BaCl + HO.$$

Preparation.—Pure baryta is prepared by igniting, in a porcelain retort, nitrate of barium free from iron and manganese. The baryta, broken into pieces about the size of a nut, is then put into a coated glass tube and heated to low redness, while a current of oxygen gas free from carbonic acid and dried by means of quicklime, is passed over it. For the first eight minutes the gas is eagerly absorbed by the baryta. After it has begun to escape from the farther end of the tube (to which a gas delivery-tube passing under water is fitted), the stream is still kept up for the space of ten or fifteen minutes. The peroxide of barium obtained by this process is, after cooling, preserved in a bottle. In the next place, 200 grms. of water are mixed with as much hydrochloric acid as will neutralise about 15 grms. of baryta. Into this liquid, contained in a cylinder, or better, in a dish of silver or platinum kept cool by surrounding it with ice, 12 grms. of peroxide of barium, slightly moistened and rubbed up in an agate mortar, are introduced by means of a wooden spatula: on agitating or stirring the liquid with the pestle, the whole dissolves completely and without effervescence. The baryta is next precipitated by sulphuric acid, added drop by drop till slightly in excess: the presence of an excess of the acid may be known by the sulphate of barium falling down more quickly than before. 12 grms. more of the peroxide are then dissolved in the same liquid, and likewise precipitated by sulphuric acid. The liquid, which now contains hydrochloric acid, sulphuric acid, a large quantity of water, and a small quantity of peroxide of hydrogen, is next separated by filtration from the sulphate of barium, the precipitate washed with a little water, and the last wash-water retained for future washings. The filtrate is again mixed, as above, twice with peroxide of barium, and twice with sulphuric acid. The filtration is then repeated, and the process continued in the same way, till 90 or 100 grms. of the peroxide are consumed. The liquid thus obtained would, on decomposition, yield from 25 to 30 measures of oxygen gas. To separate silica, alumina, sesquioxide of iron, sesquioxide of manganese, &c., which proceed from the porcelain retort in which the nitrate of baryta was ignited, the liquid is mixed with concentrated solution of phosphoric acid (2 or 3 pts. of phosphoric acid to 100 pts. of peroxide of barium)—then surrounded with ice, and supersaturated with pounded peroxide of barium: silica and the phosphates of iron, manganese, and aluminium then separate rapidly in flakes, and must be separated from the liquid by filtration through linen, and if necessary through paper. The presence of a large quantity of sulphate of barium renders the filtration difficult. (If no phosphoric acid were present, the sesquioxides of iron and manganese would fall down by themselves, and give rise to a rapid evolution of oxygen gas; but when they are mixed with phosphoric acid, they do not produce this effect.) Should the liquid still contain portions of these oxides, they must be separated by the addition of a slight excess of baryta-water; whereupon, the liquid must be immediately and rapidly filtered through several filters at once, and the filters squeezed between linen to get all out. The whole of the baryta must then be separated by carefully adding sulphuric acid in very slight excess, and filtering. The filtrate now contains nothing but water, peroxide of hydrogen, hydrochloric acid, and a very little sulphuric acid. To separate the hydrochloric acid, the liquid is surrounded with ice, and mixed with sulphate of silver. In the first place, sulphate of silver, obtained by heating nitrate of silver in contact with oil of vitriol in a platinum crucible, is introduced in the form of powder into the liquid—the whole being constantly stirred till the liquid becomes clear, a sign that the hydrochloric acid is wholly or nearly precipitated. Any hydrochloric acid that may still remain must be separated by cautiously adding more sulphate of silver. If the latter has been added in excess, it must be precipitated by carefully dropping in a dilute solution of chloride of barium. The liquid should contain neither hydrochloric acid nor silver, and should therefore give no precipitate either with solution of silver or with hydrochloric acid. The chloride of silver is separated by filtration and pressure, any portion of liquid which comes through turbid being filtered over again. To remove the sulphuric acid also, and obtain a pure mixture of water and peroxide of hydrogen, the liquid is placed in a glass mortar surrounded with ice, and rubbed up with slaked baryta previously pounded and diffused through water: the baryta is added till the sulphuric acid is very nearly saturated. The liquid is then filtered, the filter pressed between linen, and baryta-water added in slight excess: this often occasions the precipitation of oxide of iron and oxide of manganese, as well as sulphate of barium; hence the filtration must be rapidly performed. The excess of baryta is removed by cautiously adding dilute sulphuric acid, so that there may be rather a very slight excess of the acid than of the baryta. The whole of the sulphuric acid may likewise be removed by means of carbonate of barium obtained in a finely-divided state by precipitation, instead of by slaked baryta and baryta-water. Finally, to separate the whole or nearly the whole of the water, the vessel containing the liquid is placed in a dish containing oil of vitriol, and the whole placed under a receiver of the air-pump: the water then evaporates before the peroxide of hydrogen. The fluid is agitated from time to time. If it should deposit flakes of silica, which give rise to the escape of oxygen gas, it must be decanted off from them by means of a siphon: if it should evolve oxygen—which it will do as soon as it is so far concentrated as to contain about 250 times its volume of oxygen—two or three drops of sulphuric acid must be added to it. The concentration must be stopped after a few days, when the liquid is brought to such a state that when decomposed it would evolve 475 volumes of oxygen gas; for this residue, if left longer in vacuo, would evaporate as a whole. The peroxide of hydrogen must be kept in long glass tubes closed with stoppers and surrounded with ice; but, even under these circumstances, it decomposes slowly and evolves oxygen gas. (Thénard.)

2. Peroxide of barium is decomposed by hydrated hydrofluoric acid or solution of hydrofluosilicic acid, the whole being kept constantly cool: in this case, insoluble fluoride of barium or double fluoride of silicium and barium separates at once. As soon as sufficient quantities of acid and peroxide of barium have been mixed, the peroxide of hydrogen, still containing a large quantity of water, is filtered from the precipitate and concentrated in vacuo over oil of vitriol. (Pelouze, *Berz. Lehrb.* i. 411.)

Properties.—Colourless transparent liquid, of specific gravity 1·452; it does not freeze at −30°; evaporates in vacuo at ordinary temperatures without decomposition, though much less readily than water; does not redden litmus, but gradually bleaches both litmus and turmeric paper; has a harsh, bitter taste, similar to that of tartar-emetic; whitens the tongue and thickens the saliva; when placed upon the hand, it instantly turns the cuticle white, and after a time produces violent itching. (Thénard.)

Peroxide of hydrogen is miscible in all proportions with *water*, part of the water freezing out on exposure to cold. A solution containing eight times its own volume of oxygen gas begins to evolve gas at 60°, and subsequently gets into a state of violent ebullition, and when this has ceased, nothing is left but water. The peroxide likewise unites with *acids*, *e.g.* phosphoric, sulphuric, hydrochloric, nitric acid, &c., forming mixtures in which it is less easily decomposible than when alone.

It is doubtful whether peroxide of hydrogen has ever been obtained quite free from water. Thénard, however, found in a specimen prepared as above described, 6·02 per cent. hydrogen, and 93·98 oxygen, the formula HO requiring 5·88 H, and 94·12 O.

Decompositions.—The second atom of oxygen is retained by the hydrogen very loosely. Under various, and often enigmatical circumstances, it separates from the water in the form of gas, the volume of which at 14° and 0·76m. bar. (29·8 inches) amounts to 475 times that of the liquid. The gas often escapes with such rapidity as to produce violent effervescence, and even explosion. Great heat is also developed, and when the experiment is made in the dark, even light is apparent.

The several modes of decomposition are as follows:—

1. In the circuit of the voltaic battery, peroxide of hydrogen, like water, is gradually resolved into hydrogen at the negative and oxygen at the positive pole—only that the proportion of oxygen is greater than in the decomposition of water. (Thénard.)

2. By a certain elevation of temperature. At freezing temperatures, peroxide of hydrogen is but very slowly decomposed; at ordinary temperatures, it merely evolves a bubble of oxygen now and then, the decomposition not being complete for months; at 20° the escape of gas becomes more perceptible. By suddenly raising the temperature to 100°, this gradual escape of gas may be converted into a kind of explosion. Finally, there remains behind nothing but pure water. Sunshine does not appear to accelerate the decomposition at ordinary temperatures. (Thénard.)

3. By contact with certain substances, which either remain unaltered, or take up part of the oxygen of the peroxide, or on the contrary themselves evolve oxygen.—The rapidity with which these substances induce the separation of oxygen from the peroxide depends partly on their chemical nature, partly on the minuteness of their mechanical division: the further this is carried, the more rapid is the action. (Thénard.)

a. Peroxide of hydrogen, whether pure or in aqueous solution, acts as a powerful oxidising agent. It converts arsenious acid into arsenic acid, sulphurous acid into sulphuric acid, sulphide of lead into sulphate of lead, and the hydrated protoxides of manganese, iron and cobalt, into the peroxide and sesquioxides respectively. The protoxides of barium, strontium, and calcium are transformed into the corresponding peroxides, which, being insoluble, are precipitated. The concentrated solution of peroxide of hydrogen acts with great violence upon certain of the elements, selenium, arsenic, molybdenum, chromium, &c., converting them at once into their highest oxides.

b. Certain bodies, among which are included charcoal, many metals, and some metallic oxides, induce, by their mere contact, a more or less violent decomposition of the peroxide into water and oxygen, without themselves undergoing any change: gold, platinum, and silver, particularly when in the precipitated or spongy state, act most violently, and cause a great disengagement of heat. A slightly acid solution of the peroxide is less amenable to the action of these agents than is the pure aqueous solution; alkalis on the other hand facilitate the decomposition. The action of the above-mentioned bodies in causing the decomposition of the peroxide is termed catalytic. Its nature, however, is not at present understood.

c. But the most remarkable circumstance connected with peroxide of hydrogen is its property of acting as a reducing agent. When peroxide of hydrogen, or its analogue, peroxide of barium, is added to any one of the following substances, namely, the protoxides of silver or mercury, the peroxides of manganese or lead, the chromic, permanganic, and ferricyanic acids, or their salts, not only is oxygen evolved from the peroxide of hydrogen, but also from the other oxidised body. Several of these reactions were noticed by Thénard in 1818, but they were first minutely examined and explained by Brodie in 1850 (Phil. Trans. 1850, p. 759; Chem. Soc. Qu. J. iv. 194; further, Chem. Soc. Qu. J. vii. 304). In accordance with his views, it seems that the second atom of oxygen in the peroxides of hydrogen and barium is not merely retained in an unstable state of combination, but that it is, by association with the oxide of an electro-positive element, like hydrogen or barium, thrown into a polar state, opposite to the polar state of the oxygen in unstable protoxides, and to that of the loosely combined oxygen in the more or less chlorous peroxides. Hence when the peroxide of hydrogen or barium is brought into relation with one or other of these oxygenised compounds, the two oppositely polarised oxygens unite with one another, as indicated in the following formulæ:—

$$\overset{+}{Mn^2}\overset{-}{O}\overset{-}{O} + \overset{+}{H^2}\overset{-}{O}\overset{+}{O} = \overset{+}{Mn^2}\overset{-}{O} + \overset{+}{H^2}\overset{-}{O} + \overset{+}{O}\overset{-}{O}$$

$$\overset{+}{Ag}\overset{-}{Ag}\overset{-}{O} + \overset{+}{H^2}\overset{-}{O}\overset{+}{O} = \overset{+}{Ag}\overset{-}{Ag} + \overset{+}{H^2}\overset{-}{O} + \overset{+}{O}\overset{-}{O}$$

$$\overset{+}{Cr^4}\overset{-}{O^3}\overset{-}{O^3} + \overset{+}{H^6}\overset{-}{O^3}\overset{+}{O^3} = \overset{+}{Cr^4}\overset{-}{O^3} + 3\overset{+}{H^2}\overset{-}{O} + 3\overset{+}{O}\overset{-}{O}$$

$$\overset{-}{I^2} + \overset{+}{H^2}\overset{-}{O}\overset{+}{O} = 2\overset{+}{H}\overset{-}{I} + \overset{+}{O}\overset{-}{O}$$

Brodie has shown that, in the third and fourth reactions, the amounts of oxygen set free correspond exactly with the above expressions. In the other two reactions, some additional oxygen is set free catalytically, from the decomposition of the peroxide *per se*. For finely-divided metallic silver has the property of decomposing peroxide of hydrogen catalytically, whence the oxygen liberated according to the second equation has not been found to constitute more than 49, instead of 50, per cent. of the total quantity of oxygen evolved. It is observable that in no case can the oxygen from the peroxide constitute less than one-half of the total oxygen liberated. The above reactions are perfectly comparable with admitted reactions showing the formation of hydrogen and the alcohol-radicles (see Chemical affinity i. 857), for example:—

$$\overset{+}{Cu^2}\overset{-}{H} + \overset{+}{H}\overset{-}{Cl} = \overset{+}{Cu^2}\overset{-}{Cl} + \overset{+}{H}\overset{-}{H}.$$

$$\overset{+}{Zn}(C^2\overset{-}{H^5}) + (\overset{+}{C^2}H^5)\overset{-}{I} = \overset{+}{Zn}\overset{-}{I} + (C^2\overset{+}{H^5})(C^2\overset{-}{H^5}).$$

Schönbein, apparently unaware of Brodie's researches, has recently drawn attention to the phenomena of deoxidation effected by the peroxides of hydrogen and barium, and has shown that ozone is rendered inactive by them. He regards ozone as permanently negative oxygen, $\overset{-}{O}$, which can form ozonides of silver, of manganous oxide, &c., and, in the above reaction, is neutralised by the permanently positive oxygen or *antozone*, $\overset{-}{O}$, of the peroxide of hydrogen; whereas, according to Brodie, the polarity of the oxygen depends upon the nature of the body with which it is associated, and is manifested only at the instant of its disassociation. (Schönbein, Verhandl. d. naturf. Gesellsch. in Basel. ii. 113, 463, 472; Ann. Ch. Pharm. cviii. 157; J. pr. Chem. lxxvii. 257, 263; lxxx. 266, 275; lxxxi. 1; lxxxiii. 86; Jahresber. 1858, p. 58; 1859, p. 60; 1860, p. 54; 1862, p. 96.)

Schönbein has confirmed the observations of Meidinger and others, that peroxide of hydrogen may sometimes be detected in water which has undergone electrolysis. He seems also to have shown that traces of peroxide of hydrogen are produced in many cases of slow oxidation occurring in the presence of moisture; for example, those of phosphorus, ether, zinc, &c. This production of peroxide of hydrogen he considers to be correlative of the other oxidation. Thus when moist zinc-filings are oxidised by exposure to air, a quantity of peroxide of hydrogen, which may be dissolved out by water and submitted to chemical tests, is formed, according to the following equation:

$$\overset{+}{Zn}{}^2 + \overset{+}{H}{}^2\overset{-}{O} + \overset{+}{H}{}^2\overset{-}{O}\;\overset{+}{O}\overset{-}{O} = \overset{+}{Zn}\overset{+}{H}\overset{-}{O} + \overset{+}{Zn}\overset{+}{H}\overset{-}{O} + \overset{+}{H}{}^2\overset{-}{O}\overset{+}{O}.$$

Peroxide of hydrogen, even in a very dilute state, may be recognised either by its oxidising or by its reducing properties. Thus it decolorises a solution of indigo, especially in the presence of sulphate of iron, which apparently serves to convey the oxygen from the peroxide to the indigo; and similarly it liberates iodine from a solution of iodide of potassium, starch, and sulphate of iron. On the other hand, it decolorises a solution of permanganate of potassium by reduction, and causes a blue precipitate in a solution containing sesquichloride of iron and ferricyanide of potassium. It eventually reduces chromic acid to the state of chromic hydrate, but its first action is to produce, by oxidation, a very unstable perchromic acid. This compound, which has a deep blue colour, is readily soluble in ether, and its ethereal solution has a certain degree of stability; so that the presence of peroxide of hydrogen in any liquid may be ascertained by mixing it with ether, and then adding a few drops of a solution of chromic acid, whereby the ether assumes a bright blue colour.

The compound radicle, peroxide of hydrogen HO, is equivalent to the simple radicle chlorine Cl, and in a great number of reactions is exchangeable for chlorine and its congeners. One of the most generally useful modes of oxygenating different compounds consists in first substituting a halogen in exchange for hydrogen, and then, by means of water, substituting peroxide of hydrogen in exchange for the halogen. Thus, by the action of bromine upon acetic acid, we obtain bromacetic acid:—

$$C^2H^4O^2 + Br^2 = C^2H^3BrO^2 + HBr.$$

Then, by the action of water upon bromacetic acid, we obtain glycollic, or oxyacetic acid:—

$$C^2H^3BrO^2 + H.HO = C^2H^3(HO)O^2,\ \text{or}\ C^2H^4O^3 + HBr.$$

(*Odling's Manual of Chemistry*, p. 124.)

Trioxide of Hydrogen. H^2O^3.—This, according to Baumert (Pogg. Ann. lxxxix. 38), is the composition of OZONE (*q. v.*)

HYDROGEN, PHOSPHIDES OF. Three of these compounds are known, viz. phosphoretted hydrogen gas, PH^3, liquid phosphide of hydrogen, PH^2, and the solid phosphide, P^4H.

1. **Phosphoretted Hydrogen** or **Phosphamine.** PH^3.—This gas, the analogue of ammonia, is produced by the spontaneous decomposition of phosphorised organic bodies, decaying fish for example. Its natural evolution appears to be the cause of *ignes fatui* and similar luminous appearances. The gas is also liberated in many chemical reactions, but it is very difficult to obtain pure, being always mixed with a greater or lesser proportion of free hydrogen, and frequently with the vapour of liquid phosphide of hydrogen, which renders it spontaneously inflammable, a property which it does not possess when free from the liquid phosphide. The spontaneously inflammable gas was discovered in 1789 by Gengembre (Crell. Ann. i. 450), and the non-spontaneously inflammable gas by Davy some years later.

Production of the spontaneously inflammable gas. 1. The compounds of phosphorus with the alkali-metals are resolved, in contact with water, into an alkaline hypophosphite and phosphoretted hydrogen. An impure phosphide of calcium is generally used for the purpose, prepared by heating phosphorus with lime (i. 719). When it is thrown into water, spontaneously inflammable phosphoretted hydrogen is slowly liberated, and the bubbles of gas, as they reach the surface, take fire, burn with a highly luminous flame, and produce thick clouds of white smoke, which, in a quiet atmosphere, ascend in the form of successive gradually expanding rings.

2. Phosphide of zinc, tin, or iron, with aqueous sulphuric or hydrochloric acid, yields a metallic sulphate or chloride and phosphoretted hydrogen gas.

3. Phosphorus heated in an aqueous solution of a fixed alkali, yields phosphoretted hydrogen gas, together with a hypophosphite and phosphate of the alkali-metal. Such an action is exerted by potash, soda, lithia, baryta, strontia, and lime, and, according to Raymond, by oxide of zinc and protoxide of iron. The primary decomposition yields phosphoretted hydrogen and hypophosphite; thus with lime-water:—

$$\underset{\substack{\text{Hydrate of}\\ \text{calcium.}}}{3CaHO} + P^4 + 3H^2O = \underset{\substack{\text{Hypophos-}\\ \text{phite of cal-}\\ \text{cium.}}}{3CaH^2PO^2} + PH^3$$

But from the very beginning of the action, the phosphoretted hydrogen gas is mixed with more or less free hydrogen, and there is likewise a certain quantity of phosphate produced; and as the boiling is continued and the solution becomes more concentrated, the quantity of hydrogen gas continually increases, because a greater and greater quantity of the alkaline hypophosphite is resolved, by boiling in the alkaline liquid, into hydrogen and an alkaline phosphate, *e.g.*:

$$\underset{\text{Hypophosphite of potassium.}}{KH^2PO^2} + 2KHO = \underset{\text{Phosphate of potassium.}}{K^3PO^4} + H^4.$$

This secondary decomposition takes place especially with the hypophosphites of the true alkali-metals; hence solutions of the alkaline earths are best adapted for the preparation of pure phosphoretted hydrogen.

4. When hypophosphites are heated, phosphoretted hydrogen is evolved, generally of the more inflammable, more rarely of the less inflammable variety, mixed with a certain quantity of vapour of phosphorus and free hydrogen gas. (H. Rose.)

The non-spontaneously inflammable gas is produced—1. When hypophosphorous or phosphorous acid is heated, these acids being then resolved into phosphoric acid and phosphoretted hydrogen, which may be collected over water:

$$\underset{\text{Hypophosphurous acid.}}{2H^3PO^2} = PH^3 + H^3PO^4.$$

$$\underset{\text{Phosphorous acid.}}{4H^3PO^3} = PH^3 + 3H^3PO^4.$$

According to Dumas and H. Rose, the first portions of gas evolved by this process are pure, but the later portions contain a considerable quantity of free hydrogen. The phosphorous acid should be gently heated in a flask of hard glass, as when softer glass is used, a phosphite of alkali-metal is frequently formed, which is decomposed by the heat and yields free hydrogen. The mixture of phosphorous and phosphoric acids, sometimes called *phosphatic acid*, which is produced when phosphorus is left to oxidise slowly in moist air, may be used for the purpose. By the application of a stronger heat, hypophosphites, as well as hypophosphorus itself, yield phosphoretted hydrogen, but the gas produced from the salts is usually spontaneously inflammable and mixed with free hydrogen.—2. When zinc or iron is dissolved in aqueous phosphorous acid, or zinc in a mixture of aqueous phosphorous acid and sulphuric acid, or when phosphoric acid is deoxidised by potassium or sodium (Wöhler).—3. When phosphorus is boiled with hydrate of potassium and alcohol, the non-inflammable gas is evolved, mixed with hydrogen gas and alcohol vapour, and there remains hypophosphite of potassium and a small quantity of phosphate, together with excess of potash (H. Rose).—4. When phosphide of calcium is decomposed by concentrated hydrochloric acid (Dumas).—5. Phosphorus, under the influence of light, decomposes water, producing phosphoric oxide [? red phosphorus] and phosphoretted hydrogen gas, which remains dissolved in the water.

Spontaneously inflammable phosphoretted hydrogen may be freed from the compound PH^2, and rendered non-inflammable, by passing it through a freezing mixture of ice and salt; but according to Graham, the addition of a minute quantity of nitric oxide gas will confer on it the property of spontaneous inflammability [? by oxidising a small quantity of it to PH^2]. It is also deprived of its spontaneous inflammability by exposure to sunlight, by contact with charcoal and other pulverulent bodies, and by admixture with the vapours of ethylic chloride, ethylic oxide, alcohol, turpentine, &c.

Properties. Phosphoretted hydrogen is a colourless gas of specific gravity 1·214 referred to air, or 17·25 referred to hydrogen (Dumas); by calculation for a condensation to 2 volumes it is $\frac{31 + 3}{2} = 17$. It is liquefiable, but has not yet been solidified (p. 98). It smells like stinking fish, or rather the fish in a state of decomposition have the odour of the gas, since they evolve it. It is sparingly soluble in water, more so in alcohol, ether, and volatile oils. Neither the gas nor its solutions have any action upon blue or red litmus paper.

Decompositions.—1. When a series of *electric sparks* is passed through the gas, two volumes of it are converted, with deposition of phosphorus, into three volumes of hydrogen.—2. Most *metals* heated in the gas combine with the phosphorus, and liberate the hydrogen.—3. Phosphoretted hydrogen is very inflammable, burning with a brilliant flame and evolving a white smoke of phosphoric acid. A mixture of the non-spontaneously inflammable gas and *oxygen* standing over water is gradually absorbed, with production of phosphorous acid. The mixture of the two gases, though changing very gradually at ordinary pressures, undergoes, when suddenly rarefied, an instantaneous decomposition, attended with violent explosion.—4. Phosphoretted hydrogen quickly reduces many oxidised bodies, *e.g. nitric oxide, nitric acid, sulphurous anhydride* and *sulphuric acid.* It is completely absorbed by solutions of *hypochlorous acid* and the alkaline hypochlorites.—5. It precipitates the solutions of many *metallic salts* those of *lead* very slowly, those of *copper* more quickly, and those of the *noble metals* most quickly of all. The precipitates, save those produced with mercury-salts, are black or dark-coloured. They consist of metallic phosphide, as in the case of copper; of mixed phosphide and metallic salt, as in the case of mercury; or of reduced metal, as in the case of silver and gold. Solution of sulphate of copper is often used for estimating the proportion of free hydrogen in ordinary phosphoretted hydrogen, by observing the quantity of gas which it leaves unabsorbed.

6. *Chlorine, bromine,* and *iodine* decompose phosphoretted hydrogen, abstracting its hydrogen. If in excess, they also combine with its phosphorus to form the respective chlorides, bromides, and iodides, or their products of decomposition with water. When bubbles of phosphoretted hydrogen are introduced into a receiver of chlorine, they inflame with a sharp explosion, producing hydrochloric acid and pentachloride of phosphorus. Many metallic chlorides also, when gently heated in phosphoretted hydrogen, produce hydrochloric acid gas—the volume of which is three times as great as that of the phosphoretted hydrogen—and a metallic phosphide; or else hydrochloric acid, free phosphorus and free metal.—6. *Sulphur* heated in phosphoretted hydrogen forms sulphide of hydrogen and sulphide of phosphorus.

Phosphoretted hydrogen, though devoid of any alkaline reaction, is in other respects closely analogous to ammonia; hence it is called phosphamine. Thus it unites directly with *hydriodic acid* to form the hydriodate of phosphamine, $PH^3.HI$, or iodide of phosphonium, PH^4I, and a corresponding compound with *hydrobromic acid.* Moreover, like ammonia, phosphamine unites with the perchlorides of many metals, forming white saline bodies of similar constitution to the ammonio-chlorides.

Hydriodate of Phosphamine may be obtained by the direct combination of the two gases, or by adding a little water to equal atomic proportions of iodine, ground up with pounded glass, and phosphorus cut up into small pieces. Vapours of hydriodate of phosphamine mixed with hydriodic acid are immediately given off, the former condensing as a crystalline deposit. A better mode of preparation is, however, that given by Hofmann, which consists in gently heating iodine in a current of dry phosphoretted hydrogen gas:

$$4PH^3 + I^5 = PI^2 + 3H^4PI.$$

The salt crystallises in cubes, which fuse when moderately heated, and out of access of air, may be sublimed without change. They are deliquescent and are decomposed by water into hydriodic acid and phosphamine.

Hydrobromate of Phosphamine, $PH^3.HBr$ or PH^4Br, is also obtained by direct combination, or it may be prepared by introducing bromide of silicon, together with a little water, into a jar of phosphoretted hydrogen (Serullas). It crystallises in cubes, sometimes transparent, sometimes opaque; boils at about 30°. Vapour-density, obs. = 1·906; calc. (2 vol.) = 3·98; hence this compound affords an example of anomalous vapour-density, probably arising from disassociation (i. 469; ii. 816).

Derivatives of Phosphamine.—The three atoms of hydrogen, like those of ammonia, in phosphamine, may be replaced by metals or organic radicles, *e.g. tricupric phosphide,* PCu^3; *tricuprous phosphide,* PCu^6 or $PCcu^3$; *triethylphosphine,* $P(C^2H^5)^3$. The metallic phosphamines are obtained by passing phosphoretted hydrogen gas over the heated metals or their oxides, or into solutions of the respective salts, or by treating the metals directly with phosphorus. (See PHOSPHIDES.)

The organic derivatives of phosphamine constitute a more important class of compounds, exactly analogous to the tertiary monamines (i. 175). Phosphorus-bases analogous to the primary and secondary monamines have not yet been obtained. The tertiary phosphines are obtained by decomposing the zinc-compounds of the alcohol-radicles with trichloride of phosphorus, *e.g.*:

$$\underset{\text{Zinc-ethyl.}}{3C^2H^5Zn} + PCl^3 = 3ZnCl + \underset{\text{Triethyl-phosphine.}}{P(C^2H^5)^3}.$$

They are volatile strongly basic compounds, which unite readily with acids, forming crystalline salts, analogous to those of triethylamine, &c. Triethylphosphine (like triethylamine) unites directly with iodide of ethyl, forming the iodide of tetrethylphosphonium, $P(C^2H^5)^4I$, from which, by the action of moist oxide of silver, the hydrate of tetrethylphosphonium, $P(C^2H^5)^4HO$, may be obtained. (See PHOSPHORUS-BASES.)

Liquid Phosphide of Hydrogen. This compound, which communicates spontaneous inflammability to phosphoretted hydrogen gas, was discovered by Paul Thénard (Ann. Ch. Phys. [3] xiv. 5), and regarded by him as PH^2. By some chemists, however, it is supposed to contain oxygen as well as hydrogen, and to constitute the hydrogen representative of oxychloride of phosphorus, namely, H^3PO. It is produced, together with spontaneously inflammable phosphoretted hydrogen gas, by the action of water on phosphide of calcium (i. 719):

$$5PCa^2 + 5H^2O = 5Ca^2O + 5PH^2$$ (P. Thénard),

and may be separated by passing the gas through a U-tube cooled by a freezing mixture.

Into the middle tubulure of a three-necked Woulfe's bottle, holding about a pint, is inserted a glass tube 12 inches long and half an inch wide, so as to reach nearly to the bottom. To the second tubulure is adapted a tube twice bent at right angles; this tube dips into water and serves for a safety-tube. Into the third is fitted a U-tube of ¼ inch diameter, immersed to the depth of 5 or 6 inches in a freezing mixture. The part which projects above the freezing mixture is bent at a not very acute angle, and drawn out at two points not far from each other and near the end, so that, at the conclusion of the operation, the liquid may be introduced into the intermediate part of the tube, and the parts which have been drawn out closed by the blowpipe. The apparatus being thus arranged, the bottle is three parts filled with water and placed in a water-bath heated to between 60° and 70°; the last-mentioned tube is closed; and a few drops of phosphide of calcium are thrown through the middle one into the bottle. The gas evolved takes fire, and drives out the air through the safety-tube. The U-tube is now to be opened, and from 400 to 600 grains of phosphide of calcium gradually introduced into the bottle: in a few minutes, oily drops of liquid are seen to collect in the part of the tube nearest to the bottle. The process must be stopped after 15 or 20 minutes, because water condenses in the tube, together with the phosphide of hydrogen, and often stops it. The tube is now to be sealed at the narrowed neck nearest to its extremity, then removed from the bottle, and held by the finger (covered with caoutchouc to save the operator from being burnt) in such a position that any remaining gas may escape; it is then warmed by the hand to cause the portions of liquid which have been separated by particles of ice to run together, and again placed in the freezing mixture to solidify the water, and prevent it running back. This being effected, the liquid is made to flow towards the sealed end of the tube, and the other neck of the tube is closed by the blow-pipe. A well-conducted operation yields about 30 grains of liquid.

Liquid phosphide of hydrogen is colourless and does not solidify at −20°; at 30° or 40°, it appears to volatilise and to be decomposed at the same time; refracts light strongly. It is insoluble in water. Alcohol and oil of turpentine appear to dissolve it, but it quickly decomposes in the solution. It burns spontaneously in the air, with an intensely bright white flame, and produces dense white fumes. It communicates spontaneous inflammability to 500 times its weight of phosphoretted hydrogen gas. All combustible gases are rendered spontaneously inflammable by admixture with liquid phosphide of hydrogen.

By the action of light it is resolved into solid and gaseous phosphide of hydrogen, $5PH^2 = P^2H + 3PH^3$. It is also decomposed, like peroxide of hydrogen, by contact with various substances. An indefinite quantity of liquid phosphide of hydrogen may be decomposed by a cubic centimetre of hydrochloric acid gas.

Solid Phosphide of Hydrogen. P^2H?—When spontaneously inflammable phosphoretted hydrogen is exposed to sunshine, a solid yellowish compound is deposited on the sides of the glass, the gas at the same time losing its property of spontaneous inflammability (Leverrier, Ann. Ch. Phys. lx. 175). The same solid compound is obtained in larger quantity by treating liquid phosphide of hydrogen with hydrochloric acid, or by dissolving phosphide of calcium in strong hydrochloric acid, the liquid phosphide being then resolved into the solid and gaseous phosphides (see above). Hence spontaneously inflammable phosphoretted hydrogen passed through aqueous hydrochloric acid loses its spontaneous inflammability and yields a deposit of solid phosphide.

This compound is insoluble in water and in alcohol. It dissolves in warm potash, with liberation of non-spontaneously inflammable phosphoretted hydrogen. It takes fire at about 150°. (P. Thénard, *loc. cit.*)

HYDROGEN, SELENIDE OF. H^2Se. *Selenhydric* or *Hydroselenic acid. Seleniated Hydrogen.*—A gaseous compound analogous to sulphydric acid, produced by the action of dilute hydrochloric or sulphuric acid on selenide of potassium, iron, or other metals. It is colourless and inflammable, soluble in water, and cannot long be preserved over mercury. It has a most offensive, acrid odour, impairing or even destroying the sense of smell for several hours, and producing inflammation of the eyes. Its aqueous solution absorbs oxygen from the air, and deposits selenium. It has a hepatic taste, a slight acid reaction, and gives with the solutions of most metals, precipitates consisting of metallic selenides, those of manganese, zinc, and cerium being flesh-coloured, the remainder brown or black. (Berzelius.)

HYDROGEN, SULPHIDES OF. Sulphur unites with hydrogen in two proportions, forming the protosulphide, H^2S; and the persulphide, probably HS or H^2S^2.

Protosulphide of Hydrogen. H^2S. *Sulphydric acid. Hydrosulphuric acid. Hydrothionic acid. Sulphuretted hydrogen.*—This compound may be formed in small quantity by burning sulphur-vapour in hydrogen gas, or hydrogen gas in sulphur-vapour, precisely as its analogue, water, is produced under similar circumstances from oxygen and hydrogen.

The gas is ordinarily prepared by the action of an acid—sulphuric or hydrochloric for instance—upon a metallic sulphide, usually that of iron or antimony. Dilute sulphuric acid acts readily upon sulphide of iron, producing, even in the cold, a rapid effervescence of sulphydric acid:

$$Fe^2S + H^2SO^4 = H^2S + Fe^2SO^4.$$

Inasmuch as sulphide of iron is an artificial product, nearly always containing an excess of metallic iron in admixture, the sulphydric acid obtained from it is generally contaminated with free hydrogen; but the native crystalline trisulphide of antimony, being a normal sulphide, when acted upon by boiling hydrochloric acid, yields the gas in question in a very pure state, thus:

$$Sb^2S^3 + 6HCl = 3H^2S + 2SbCl^3.$$

The sulphydric acid obtained from either of these sources may be passed through a small quantity of water to wash it, and over chloride of calcium to render it dry. It may be collected in the gaseous state over mercury, or absorbed at once into water, in which it is very soluble.

Sulphydric acid, more frequently sulphydrate of ammonia, results from the spontaneous decomposition of sulphuretted organic compounds; also from treating non-sulphuretted organic compounds with sulphur. Reinsch recommends a laboratory process for obtaining pure sulphydric acid, by heating in a glass flask a mixture of equal parts of sulphur and suet.

Sulphydric acid occurs naturally, and is not unfrequently evolved from fumaroles and volcanoes. It exists to a considerable extent in certain mineral waters known as hepatic waters, those of Harrogate, for instance. It is also produced spontaneously in many waters charged with organic matter and sulphates, usually sulphate of calcium.

Properties.—At ordinary temperatures and pressures, sulphydric acid is gaseous. It may be obtained in the liquid state by generating it in one limb of a sealed tube, from sulphuric acid and sulphide of iron freed from metallic iron, and condensing it in the other limb, which should be immersed in a freezing mixture, that of ice and salt being sufficient for the purpose; or liquid persulphide of hydrogen may be gently heated in one limb of a bent sealed tube, when it breaks up into sulphur, which remains, and sulphydric acid, which may be condensed in the other limb kept cool for the purpose. By the powerful refrigeration resulting from the evaporation *in vacuo* of a mixture of solid carbonic anhydride and ether, it may be solidified. Solid sulphydric acid, or sulphur-ice, is a white transparent mass which melts at $-85 \cdot 5°$. Liquid sulphydric acid is a colourless transparent fluid, remarkable for its extreme thinness or mobility. Its specific gravity is 0·9 compared with that of water as 1. Sulphydric acid gas is transparent and colourless. Its density is somewhat greater than that of atmospheric air, being 1·1781 referred to air, or 17 referred to hydrogen, as unity. It is characterised by an offensive odour resembling that of rotten eggs, the smell of which indeed is due to the evolution of this gas, or of its compound with ammonia. In the concentrated state it cannot be breathed with impunity, and even when much diluted it frequently gives rise to nausea and vertigo. An atmosphere containing $\frac{1}{10}$ per cent. of this gas proves fatal to the lower animals.

Sulphydric acid is readily inflammable. It burns with a bluish flame, forming sulphurous acid, and frequently deposits free sulphur from the imperfect access of oxygen. Most *metals* when heated in the gas absorb the sulphur and leave the hydrogen. *Cadmium* or *tin* is generally used for the purpose: $Cd^2 + H^2S = Cd^2S + H^2$. The bulk of the resulting hydrogen is equal to that of the original sulphydric acid; or, in other words, two volumes of sulphydric acid, H^2S, when acted on by metal, leave two volumes of hydrogen. Sulphydric acid in the gaseous state, or dissolved in water, is decomposed by *chlorine*, *bromine*, and *iodine*, with liberation of sulphur and formation of hydrochloric, hydrobromic, and hydriodic acids respectively. In a similar manner it is decomposed, with liberation of sulphur, by nearly all *oxidising agents;* and even *sulphurous acid*, which usually acts as a deoxygenant by absorbing oxygen, acts in this case as an oxygenant by affording oxygen:

$$2H^2S + SO^2 = 2H^2O + S^3.$$

In some cases, however, a peculiar sulphur-acid, the pentathionic, is formed in addition, thus:

$$5H^2S + 5SO^2 = 4H^2O + H^2S^5O^6 + S^5.$$

A saturated aqueous solution of sulphydric acid contains about three times its volume of the gas. It is a clear colourless liquid, having a slight acid reaction, and the smell and taste of the gas. It is gradually decomposed by exposure to air, its hydrogen being oxidised into water and its sulphur set free. Sulphydric acid when burnt yields sulphurous acid, as we have seen; but moist sulphydric acid, mixed with air or oxygen, and exposed to a moderately warm temperature, from 40° to 90°, is converted into sulphuric acid.

Sulphydric acid, like water, is capable of giving up the half or the whole of its hydrogen in exchange for a metal, the resulting compound being a sulphydrate or a sulphide, according as 1 or 2 at. H are thus replaced; *e. g. sulphydrate of barium*, BaHS; *sulphide of barium*, $\mathrm{Ba^2S}$. It is only the alkali-metals and alkaline-earth-metals that appear to be capable of forming definite sulphydrates, all of which are soluble in water and crystallisable. The heavy metals form insoluble sulphides, which may be derived from a single or a multiple molecule of sulphydric acid, just as the corresponding oxides are derived from a single or multiple molecule of water: *e. g. sulphide of silver*, $\mathrm{Ag^2S}$; *mercuric sulphide*, $\mathrm{Hg^2S}$ or $\mathrm{Hhg''S}$; *trisulphide of antimony*, $\mathrm{Sb^2S^3}$, &c. (See SULPHIDES and SULPHYDRATES.)

The sulphides of the heavy metals are precipitated from solution of metallic salts by sulphydric acid or an alkaline sulphide or sulphydrate:

$$\begin{array}{ccccccccc} \mathrm{Cu^2SO^4} & + & \mathrm{H^2S} & = & \mathrm{H^2SO^4} & + & \mathrm{Cu^2S.} \\ \mathrm{2SbCl^3} & + & \mathrm{3H^2S} & = & \mathrm{6HCl} & + & \mathrm{Sb^2S^3.} \\ \mathrm{Fe^2SO^4} & + & \mathrm{NH^4.H.S} & = & \mathrm{NH^4.H.SO^4} & + & \mathrm{Fe^2S.} \end{array}$$

Some metals are precipitated in this manner from their acidified solutions by sulphydric acid gas or its aqueous solution; others only from neutral or nearly neutral solutions, by an alkaline sulphide or sulphydrate, in some cases as sulphides (nickel, cobalt, manganese, zinc, uranium), in others as hydrates (chromium, and the metals of the earths proper); and and lastly, there are some metals, namely those of the alkalis and alkaline earths, which are not precipitated either by sulphydric acid or an alkaline sulphydrate. On these reactions is founded a division of the metals into groups, which forms the basis of the mode of separating them usually adopted in analysis. (See ANALYSIS, INORGANIC, i. 217.)

Sulphydric acid is recognised by the black discoloration it produces on paper moistened with solutions of lead or bismuth, and by the black tarnish it gives to silver-foil.

Persulphide of Hydrogen. $\mathrm{H^2S^2}$?—This compound seems to be the sulphur-representative of peroxide of hydrogen, which it much resembles in its properties. It is made by gradually adding the solution of a persulphide of alkaline earth- or alkali-metal to an excess of hydrochloric acid diluted with twice its bulk of water:

$$\mathrm{Ca^2S^5} + \mathrm{2HCl} = \mathrm{2CaCl} + \mathrm{H^2S^2} + \mathrm{S^3}.$$

The persulphide of hydrogen is formed without any evolution of gas, and separates as a yellowish oily fluid, heavier than water. It has the property of dissolving sulphur to a considerable extent, owing to which circumstance its composition has not been satisfactorily established. Persulphide of hydrogen has a peculiar, sulphurous, disagreeable odour. It produces superficial white eschars on the skin and mouth. It is insoluble in water, but soluble in ether, forming a solution which soon decomposes and deposits crystals of sulphur. It is readily inflammable, and burns with a blue flame. It is possessed of bleaching properties analogous to those of peroxide of hydrogen.

Persulphide of hydrogen is a very unstable substance, and, especially at increased temperatures, undergoes spontaneous decomposition into sulphydric acid and sulphur. By effecting this decomposition in a sealed tube, liquid sulphydric acid may be obtained (p. 203). The stability of the persulphide is increased by the presence of moderately strong acids. Alkalis, on the other hand, promote its decomposition. Hence if, in its preparation, the hydrochloric acid be added to the alkaline persulphide, instead of the persulphide to the acid, no persulphide of hydrogen, but only sulphydric acid and sulphur will be obtained. Under the influence of catalytic agents, such as finely-divided platinum, gold, iridium, and charcoal, which effect the similar decomposition of peroxide of hydrogen into oxygen and water, persulphide of hydrogen undergoes an instantaneous decomposition into sulphur and sulphydric acid. It reduces peroxide of manganese and the oxides of silver and gold, the last two with great violence, and frequently even with ignition. (*Odling's Manual of Chemistry.*)

HYDROGEN, TELLURIDE OF. $\mathrm{H^2Te}$. *Tellurhydric* or *Hydrotelluric acid. Telluretted hydrogen.*—This compound is evolved as a gas, when certain metallic tellurides, the telluride of zinc being generally used, are treated with hydrochloric acid:

$$\mathrm{Zn^2Te} + \mathrm{2HCl} = \mathrm{H^2Te} + \mathrm{2ZnCl}.$$

It closely resembles its analogues, sulphydric and selenhydric acids, smells very much like the former, burns with a blue flame, has a slight acid reaction, and dissolves in water, forming a colourless liquid which deposits tellurium when exposed to the air. It precipitates most metals from their solutions in the form of tellurides (*q. v.*)

HYDROHALITE. A native hydrated chloride of sodium, $NaCl.2H^2O$. (Dana, ii. 506.)

HYDROKINONE. See Hydroquinone.

HYDROLEIC ACID. See Oleic acid.

HYDROLITE. Syn. with Gmelinite (ii. 924).

HYDROMAGNESITE. *Hydrated carbonate of magnesium*, $4Mg^2O.3CO^2.4H^2O = 3(Mg^2CO^3.H^2O).2MgHO$ or $3(Mg^2H^2CO^4).2MgHO$.—It occurs native in small monoclinic crystals, usually acicular or bladed and tufted, also amorphous or as a chalky crust. Specific gravity = 2·145. Hardness of crystals = 3·5. Lustre vitreous to silky or sub-pearly; also earthy. Colour and streak white. It is found in serpentine at Hrubschitz in Moravia; near Kumi in Negroponte; at Hoboken, New Jersey, and other localities in North America (Dana, ii. 457). A specimen from Texas, Lancaster county, Pennsylvania, analysed by Smith and Brush (Sill. Am. J. [2] xv. 207), gave 36·00 per cent. CO^2, 43·96 Mg^2O, 19·68 water, and 0·36 silica. Artificially prepared hydrocarbonate of magnesium has sometimes the same composition.

HYDROMAGNOCALCITE. Syn. with Hydrodolomite.

HYDROMARGARIC and **HYDROMARGARITIC ACIDS.** Acids of doubtful constitution, which Frémy obtained by treating olive-oil with strong sulphuric acid. (See Margaric acid and Palmitic acid.)

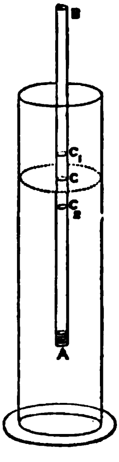
HYDROMELLONE. See Mellone.

HYDROMETER (ὕδωρ, water; μέτρον, measure). *Gravimeter*, *Pése-liqueur*; on the Continent, most commonly called the *Areometer* (ἀραιὸς, rare, subtle). An instrument which, on being placed in a liquid, shows its specific gravity, either by direct inspection, or by simple adjustment and calculation.

Its action depends on the simple principle of hydrostatics, that a floating body must displace its own weight of liquid. The truth of this principle is seen if we consider that any part of a mass of liquid at rest must be supported by the pressure of the surrounding liquid, and will certainly continue to be supported, so long as it has the same weight and volume: hence it may be conceived to become solid without altering the conditions of equilibrium. Now weight is mere downward pressure, and the solid immersed in a liquid need not weigh so much as an equal volume of liquid, provided that the difference is exactly made up by downward pressure, or weight communicated from another part of the solid, above the surface of the liquid.

Thus, in *fig.* 557, suppose the solid AB to have the same weight as a volume of water equal to the volume of the part AC. When placed in water, the solid will sink up to the point C: for the upward pressure of the water, which usually supports a volume of water equal to AC, will then be exactly sufficient to support the weight of the solid AB. If we now place AB in a liquid of less specific gravity, the weight of AB will be greater than the weight of the volume AC of the liquid, and equal, for instance, to the weight of the volume AC_1. Then by similar reasoning, AB will sink into this lighter liquid up to the point C_1. Again, if AB sink in a third liquid only up to the point C_2, it is obvious as before, that the volume of liquid AC_2 is equal in weight to the solid AB.

Fig. 557.



Now the specific gravities of bodies are, by definition, in the proportion of the weights of equal volumes of the bodies, or, which is the same, in the inverse proportion of the volumes of equal weights. In other words, the specific gravity is less, as it requires a larger volume to make a given weight. Now the volumes AC, AC_1, AC_2, of the respective liquids are all of one weight, that of the solid AB: hence the specific gravities have the inverse proportion of AC, AC_1, AC_2, or if we assume the first (water) to have the specific gravity 1·00, the specific gravities of the others are $\frac{AC}{AC_1}, \frac{AC}{AC_2}$.

The hydrometers commonly used do not differ from the solid body AB above described, except that the part which meets and cuts the surface of the liquid is usually of very narrow section, in order that slight differences in the density of the liquid may cause the hydrometer to rise or sink through a considerable space. The form of those parts of the hydrometer below the liquid has no effect upon the accuracy of the result, but for convenience the lower parts are usually much expanded, in order that they may be proportionally shorter. Several different forms of the hydrometer are shown in *figs.* 558, 559, 560. The hydrometer in *fig.* 558 would indicate specific gravities differing through a considerable range, but without much accuracy. It is accompanied by a tube TB, which holds the liquid under examination. That in *fig.* 559, on the contrary, has a very slender stem (SM), and would indicate with great accuracy any specific gravities within a certain narrow range. Hydrometers are usually made of light glass tubes and bulbs blown in a single piece. The chief part of the weight is given by small shots or mercury, carefully adjusted so that the instrument shall sink to a convenient depth in the required liquids, and then sealed up in a small bulb at the lowermost extremity. In other cases, the hydrometer is made of thin gilt brass or silver, as in *fig.* 560, but the weight is still placed below, in order that the instrument may float upright and stiffly.

Fig. 558.

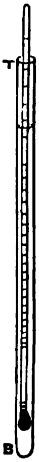


Fig. 559.

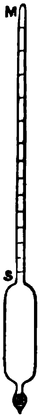


Fig. 560.

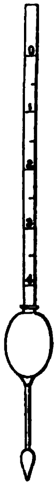
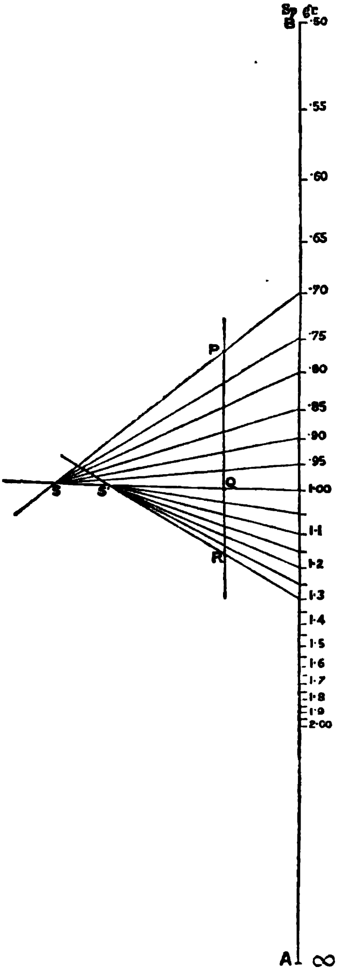


Fig. 561.



Graduation.—We have yet to consider the nature of the graduation on the stem of any hydrometer which is to give by inspection the specific gravity of the liquid in which it floats. Reverting to *fig.* 557, let the distance AC to which the hydrometer sinks be successively x_0, x_1, x_2, &c. when AB stands in liquids of the densities ρ_0, ρ_1, ρ_2, &c.

Then $\frac{x_1}{x_0} = \frac{\rho_0}{\rho_1}$, $\frac{x_2}{x_0} = \frac{\rho_0}{\rho_2}$, &c. Of these quantities let ρ_0 be the density of distilled water at the temperature 62° F., which we assume as 1·00; call the corresponding length x_0, the unit of length. Then $x_1 = \frac{1}{\rho_1}$, $x_2 = \frac{1}{\rho_2}$ &c., and $x_1 - x_2 = \frac{1}{\rho_1} - \frac{1}{\rho_2}$. Thus we see that equal differences of specific gravity are indicated, not by any equal intervals on the scale, but by the differences of the reciprocals of those specific gravities, or by quantities proportional to them. The scale which must then be employed is to be obtained by calculation, and its character is shown with some accuracy in the divided line AB *fig.* 561.

Until recently, indeed, it was customary to graduate the stem of every hydrometer into some series of equal divisions arbitrarily chosen, and the indications were either used conventionally, without reference to specific gravity at all, or the corresponding specific gravity was ascertained by calculation or reference to a table. It is obviously desirable, however, to adopt the true scale of specific gravities, since this can always be constructed with facility and sufficient accuracy.

A mode of graduating hydrometers with accuracy, as practised by Mr. Ackland, is described in the Reports of the Jurors of the Exhibition of 1851 (p. 25). It consists of the following processes:

1. Ascertaining the exact position of three or more points of the scale, according as the stem of the hydrometer is more or less truly cylindrical.

2. Dividing with great accuracy a scale on boxwood, to show the specific gravities required to be indicated by the hydrometer.

3. Making a reduced copy of the boxwood scale, so as to form a scale, the points of which shall correspond with the ascertained points on the hydrometer-tube. The scale so formed on paper is ready to be engraved on the hydrometer.

For example, suppose it be required for a hydrometer to show specific gravities from 1·00 to 0·700. A bulb is chosen with a stem as uniform as possible, and three points—for instance, ·700, ·850, and 1·000—are ascertained as follows: Load the hydrometer till it sinks in distilled water of the temperature 62° to some marked point convenient for the degree 1·00; let the weight of the instrument then be x. To ascertain the point of the degree ·85, alter the weight of the hydrometer until it is $\frac{1{\cdot}00 \times x}{{\cdot}85}$, and placing it in water, mark where it is cut by the surface. Lastly, alter the weight to $\frac{1{\cdot}00 \times x}{{\cdot}70}$, and mark the point as before, which will correspond with the specific gravity ·700. The original weight x of the hydrometer may then be restored and the tube sealed. This method, requiring the use of no liquid but water, is very convenient, and was suggested to Mr. Ackland by Dr. Clarke of Aberdeen.

The remainder of Mr. Ackland's processes are performed by calculating the reciprocals of the specific gravities required, forming them into a scale, and then reducing this scale and transferring it to the glass tube by a dividing engine of peculiar and ingenious construction.

We have formed the following table of the reciprocals, and their differences. Intermediate degrees can easily be interpolated when necessary.

Specific gravity.	Reciprocal.	Difference of Reciprocals.	Specific gravity.	Reciprocal.	Difference of Reciprocals.
2·00	·500	·013	1·25	·800	·033
1·95	·513	·013	1·20	·833	·037
1·90	·526	·015	1·15	·870	·039
1·85	·541	·015	1·10	·909	·043
1·80	·556	·015	1·05	·952	·048
1·75	·571	·017	1·00	1·000	·053
1·70	·588	·018	·95	1·053	·058
1·65	·606	·019	·90	1·111	·065
1·60	·625	·020	·85	1·176	·074
1·55	·645	·022	·80	1·250	·083
1·50	·667	·023	·75	1·333	·096
1·45	·690	·024	·70	1·429	·109
1·40	·714	·027	·65	1·538	·129
1·35	·741	·028	·60	1·667	·151
1·30	·769	·031	·55	1·818	·182
			·50	2·000	

We shall now describe a graphical method which the chemist can easily use as a substitute for Mr. Ackland's dividing engine, so as to graduate his own hydrometers with accuracy. Draw a line AB (*fig.* 561) on a sheet of good paper, and lay off upon it, with exactness, as many of the reciprocal numbers or differences, given in the table, as are likely to be required within the range of the hydrometers to be graduated: this may easily be done with the aid of a decimal or diagonal scale and a pair of compasses. The absolute size of this scale is of no importance, except that the larger it is the more accurate will the result probably be.

Now suppose the points on a hydrometer have been determined for the specific gravities ·700, 1·00 and 1·30. Draw a line exactly parallel to AB, and measure off distances PQ, QR, equal to the absolute distances of the points on the hydrometric stem, placing the points P, Q, R, as nearly as possible opposite the specific gravities ·700, 1·00, 1·30, on the scale AB. Draw lines through P and the degree ·70, and through Q and the degree 1·00. If these lines never meet, the scale on PQ will be identical with that on AB. But suppose they meet in S: draw lines through S and the several degrees on AB between ·70 and 1·00. Then the intersections of these lines and PQ give the required points for the scale PQ. Next draw a line through R and the degree 1·3. If this also pass through the point S it will indicate that the stem of the hydrometer is perfectly uniform. But wherever S′, the point of intersection of Q – 1·00 and R – 1·30 may be, draw lines from S′, through the degrees of AB, giving by their intersection with QR the required points of graduation.

If necessary, other points besides P, Q, R, might, for the sake of accuracy, be determined on the stem of the hydrometer, and the graduation could still be performed, with but little extra trouble, from many successive points of intersection.

The hydrometer scale, when once obtained on paper, can be transferred to the glass stem of the instrument by the usual process of etching with hydrofluoric acid. The glass must be covered with bees'-wax, and firmly fixed, at a proper distance, in the same straight line with the divided scale, the degrees of which may then be easily and accurately transferred by a beam-compass. For fuller directions on the method of graduating glass tubes, the reader must consult Bunsen's Gasometry (p. 25), also the article Analysis of Gases in this Dictionary (i. 269). Were it desired often to graduate hydrometers, it would be best to engrave the scale AB (*fig.* 561) upon a glass plate, together with converging lines drawn through the degrees, and then to use it as Bunsen describes.

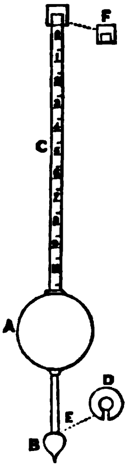
The smaller intervals of a hydrometer scale may always be subdivided into equal parts by estimation, or otherwise, without appreciable error.

The delicacy of the hydrometer may always be increased to an indefinite extent by lessening the diameter of the stem; but in the same proportion it becomes more limited in range, and troublesome to use. The adhesion of air-bubbles is a great source of discrepancy, especially in the metal instruments, and for this reason all hydrometers should be made with as smooth and small a surface as possible.

Again, the attraction of the glass or metal stem for the water causes the surface of water to rise up against the stem in a parabolic curve. This phenomenon alone, by preventing us from getting an exact reading, is almost enough to condemn the hydrometer as a standard instrument of measurement. Fortunately the hydrostatic balance and the specific gravity bottle are means of determining specific gravities with unlimited accuracy and considerable ease. The hydrometer takes a subordinate rank, and is chiefly employed in approximately determining the strength of solutions or mixtures of liquids. It often effects a wonderful saving of time or trouble, and any person frequently occupied with liquids of a variable strength or composition should have hydrometers suitably constructed in range and delicacy for testing them. To treat the instrument as suitable for exact scientific measurement, and to investigate and determine corrections for every little error which might arise, would be a mistake. We accordingly proceed to describe various well-known forms of the hydrometer, which are extensively used for practical purposes.

Sykes' *Hydrometer* is of importance because, by Act of Parliament (58 Geo. III. c. 28; see also 3 & 4 Will. IV. c. 52 § 123) it is employed in the collection of the excise revenue of the United Kingdom levied upon spirituous liquors, of which of course the strength must be determined. It is made of brass (*fig.* 562) with a spherical bulb A, 1½ inch in diameter, a weight (B) to sink it and maintain it upright in the liquor, and a flat uniform stem C, 3½ inches long, divided into ten parts, each of which is again divided into two parts. A series of nine weights of the form D accompany the instrument, having the proportions 10, 20, 30, . . . 90. These weights are placed in succession at E, until the instrument is found to sink in the liquor up to some point of the divided scale. The numerical reading of the scale at the point where it is cut by the surface of the liquor, added to the number on the weight employed, gives the required result. But the temperature of the liquor must also be observed, and the proportion of spirit it contains ascertained by a table in which the variables are the degrees of the hydrometer and thermometer.

Fig. 562.



The supernumerary weight F may be placed on the summit of the stem, and then causes the hydrometer, loaded with the circular weight 60, to sink to the same point in pure water to which it would otherwise sink in proof spirits. Concerning the determination of the proportion of alcohol contained in a mixture with water, see Alcoholometry (i. 81).

Jones' *Hydrometer* is an improvement on that of Sykes. It is accompanied by three detached weights, so that, according as these are used or not, the hydrometer may have four different degrees of weight. Corresponding to these are four separate scales on the sides of the stem, which is made square for the purpose. A thermometer, also with four different scales, is included in the lower part of the instrument, and the whole is so contrived that the number of gallons in the 100 under or over *proof* may be read off.

The following formulæ apply to any hydrometer, as for instance Sykes' or Jones', in which weights are added below the liquid.

Let w = weight of hydrometer.
v = volume of hydrometer up to the bottom of the scale.
m = area of section of stem (supposed uniform).

In liquid A let the hydrometer loaded with the weight w_1 sink to the degree x_1 (measured in inches from the bottom of scale), and in liquid B, when loaded with w_2, let it sink to x_2. Also let v_1 = volume of weight w_1.

v_2 = „ w_2.

Then the volume of A displaced is $V + v_1 + x_1.m$.

„ B „ $V + v_2 + x_2.m$.

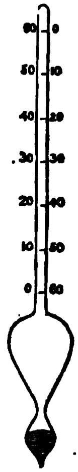
The weight of the volume of A displaced is $W + w_1$.

„ „ B „ $W + w_2$.

Then $(V + v_1 + x_1.m)$ and $(V + v_2 + x_2.m)\frac{W+w_1}{W+w_2}$ are the volumes of equal weights of A and B. And we have

$$\frac{\text{specific gravity of A}}{\text{specific gravity of B}} = \frac{(V + v_2 + x_2.m)(W + w_1)}{(V + v_1 + x_1.m)(W + w_2)}.$$

Fig. 563.



Hydrometers could easily be constructed in which weights might be added above the surface of the liquid, so that the volume of the lower parts of the instrument should not be altered. The above formula would then apply, after omission of v_1 and v_2. A hydrometer of this kind, giving any specific gravity from ·6 to 2·0, was shown in the Exhibition of 1851. (Jury Reports, p. 296.)

Baumé's *Hydrometer* is extensively employed on the Continent, and was originally described by Baumé in his *Elémens de Pharmacie*, p. 466. Separate instruments are usually constructed for liquids heavier and lighter than water, although it is obvious that this is not necessary. For liquids heavier than water, the graduation is as on the right-hand side of *fig.* 563, and is determined by marking as 0 the point to which the hydrometer sinks in pure water, and as 15 the point to which it sinks in a solution of 15 pts. by weight of salt in 85 pts. of water. The interval is divided into 15 equal parts, and a scale of similar equal parts is extended as far as desirable.

For liquids lighter than water, the graduation is as on the left-hand side of *fig.* 563. The degree 10 is now determined by pure water, while the degree 0 is the point to which the hydrometer sinks in a solution of 10 pts. of salt in 90 pts. of water. The interval is divided into 10 equal parts, and the scale is extended as in the former case.

The degrees of Baumé's hydrometers being entirely arbitrary, the following tables must be used to ascertain from their indications the specific gravities of liquids with respect to water as the standard:

Comparison of the Degrees of **Baumé's** *Hydrometer with the real Specific Gravities of liquids heavier than water.*

Degrees.	Specific gravity.	Degrees.	Specific gravity.	Degrees.	Specific gravity.	Degrees.	Specific gravity.
0	1·000	20	1·152	39	1·345	58	1·617
1	1·007	21	1·160	40	1·357	59	1·634
2	1·013	22	1·169	41	1·369	60	1·652
3	1·020	23	1·178	42	1·382	61	1·670
4	1·027	24	1·188	43	1·395	62	1·689
5	1·034	25	1·197	44	1·407	63	1·708
6	1·041	26	1·206	45	1·421	64	1·727
7	1·048	27	1·216	46	1·434	65	1·747
8	1·056	28	1·226	47	1·448	66	1·767
9	1·063	29	1·236	48	1·462	67	1·788
10	1·070	30	1·246	49	1·476	68	1·809
11	1·078	31	1·256	50	1·490	69	1·831
12	1·086	32	1·267	51	1·505	70	1·854
13	1·094	33	1·277	52	1·520	71	1·877
14	1·101	34	1·288	53	1·535	72	1·900
15	1·109	35	1·299	54	1·551	73	1·924
16	1·118	36	1·310	55	1·567	74	1·949
17	1·126	37	1·322	56	1·583	75	1·974
18	1·134	38	1·333	57	1·600	76	2·000
19	1·143						

Baumé's *Hydrometer for liquids lighter than water.*

Degrees.	Specific gravity.	Degrees.	Specific gravity.	Degrees.	Specific gravity.	Degrees.	Specific gravity.
10	1·000	23	·918	36	·849	49	·789
11	0·993	24	·913	37	·844	50	·785
12	·986	25	·907	38	·839	51	·781
13	·980	26	·901	39	·834	52	·777
14	·973	27	·896	40	·830	53	·773
15	·967	28	·890	41	·825	54	·768
16	·960	29	·885	42	·820	55	·764
17	·954	30	·880	43	·816	56	·760
18	·948	31	·874	44	·811	57	·757
19	·942	32	·869	45	·807	58	·753
20	·936	33	·864	46	·802	59	·749
21	·930	34	·859	47	·798	60	·745
22	·924	35	·854	48	·794		

Cartier's *Hydrometer* is sometimes used on the Continent. The degree of its scale 22 coincides with the degree 22 of Baumé, but above and below this point, the degrees of Baumé are diminished in the ratio of 16 to 15. This hydrometer is only constructed for liquids lighter than water, and any who may require it can easily reduce its readings to those of Baumé, and make use of the table already given for Baumé's hydrometer.

Beck's *Hydrometer* has a scale of which 0 corresponds to the specific gravity 1·00, and 30 to that of ·850, and the scale is extended in equal parts above or below 0, as far as desirable. The following tables are necessary:

Table for converting degrees of **Beck's** *Hydrometer into real Specific Gravities.*

Degrees.	Specific gravity.		Degrees.	Specific gravity.		Degrees.	Specific gravity.	
	Greater than 1·000.	Less than 1·000.		Greater than 1·000.	Less than 1·000.		Greater than 1·000.	Less than 1·000.
1	1·006	·994	25	1·172	·872	48	1·393	·780
2	1·012	·988	26	1·181	·867	49	1·405	·776
3	1·018	·983	27	1·189	·863	50	1·417	·773
4	1·024	·977	28	1·197	·859	51	1·429	·769
5	1·030	·971	29	1·206	·854	52	1·441	·766
6	1·037	·966	30	1·214	·850	53	1·453	·762
7	1·043	·960	31	1·223	·846	54	1·466	·759
8	1·049	·955	32	1·232	·842	55	1·478	·756
9	1·056	·950	33	1·241	·837	56	1·491	·752
10	1·063	·944	34	1·250	·833	57	1·504	·749
11	1·069	·939	35	1·259	·829	58	1·518	·746
12	1·076	·934	36	1·268	·825	59	1·532	·742
13	1·083	·929	37	1·278	·821	60	1·546	·739
14	1·090	·924	38	1·288	·817	61	1·560	·736
15	1·097	·919	39	1·298	·813	62	1·574	·733
16	1·104	·914	40	1·308	·810	63	1·589	·730
17	1·111	·909	41	1·318	·806	64	1·604	·727
18	1·118	·904	42	1·328	·802	65	1·619	·723
19	1·126	·899	43	1·339	·798	66	1·635	·720
20	1·133	·895	44	1·349	·794	67	1·651	·717
21	1·141	·890	45	1·360	·791	68	1·667	·714
22	1·149	·885	46	1·371	·787	69	1·683	·711
23	1·157	·881	47	1·382	·783	70	1·700	·708
24	1·164	·876						

Twaddell's *Hydrometer* is often used in England for testing liquids denser than water. It is graduated in such a manner that the reading, or number of degrees, multiplied by 5 and added to 1000, gives the specific gravity with reference to water as 1000. Thus,

10° Twaddell indicates the specific gravity 1050 or 1·050,
90° „ „ 1450 or 1·450.

(E. **Dingler**, Polytech. Jour. lxii. 329.)

Deparcieux's *Hydrometer* is an instrument with a large bulb and very narrow stem, used for determining the specific gravity of water from various springs or other sources. (**Prony's** *Architecture Hydraulique*, tom. i. § 614–627.)

The *Marine Hydrometer* is adapted to taking the specific gravity of sea-water. In *fig.* 561 is shown an accurate instrument of this kind made of gilt brass, the flat stem of which is divided into 40 parts, from 3 or more points experimentally determined. Each degree corresponds to a point in the third place of decimals; thus the degree 27 represents the specific gravity 1·027, and the whole range of the instrument is accordingly from 1·000 to 1·040.

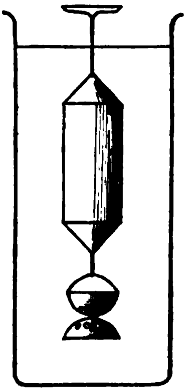
The hydrometers supplied by Government to the navy and mercantile shipping are slender glass instruments, but their accuracy is secured by comparison and determination of the error, if any, just as in the case of barometers and thermometers. They are employed in daily or hourly observations on the water of the ocean.

The *Lactometer* is a hydrometer closely resembling Sykes' hydrometer, but adapted by Dicas of Liverpool for determining the quality of milk. By means of a series of eight weights, the scale has a range of 80 degrees, and a thermometer and an ivory sliding-rule accompany the instrument in order that the milk may be tested at any temperature, and the result reduced to the standard temperature of 55° without calculation (*Brewster's Edinburgh Cyclopædia*, or *Agric. Survey of Lancashire*). This instrument must not be confused with the other lactometer first described by **Sir Joseph Banks** (*Brande's Journal*, iii. pp. 393–4), and consisting of a simple graduated test-tube, in which the new milk is allowed to stand, until the cream rises to the top and its proportional amount may be directly measured off.

Wilson's *Beads* consist of a series of little balloon-shaped glass bubbles, adjusted to certain degrees of specific gravity. When a number of them are thrown into a liquid, those which are of greater specific gravity than the liquid sink into it, those which are of less specific gravity float, while only the single bead which corresponds in specific gravity with the liquid remains indifferently in any part of the liquid, or at least sinks or rises very slowly. Upon each bead is engraved the specific gravity which it indicates. These useful little instruments were much improved and patented by Mrs. Lovi.

Fahrenheit's *Hydrometer* differs somewhat from and is even simpler than the common hydrometer. In place of a scale, it has only a single mark on the stem, but at the top of the stem is a small scale-pan on which weights are to be placed until the hydrometer sinks up to the mark in the liquid which is being tested. By this means we measure the weight of a constant volume of the liquid displaced: for this weight, by the principles of hydrostatics, is equal to the whole weight of the loaded hydrometer supported by the liquid. Hence the ratio of this weight for any given liquid to the weight for pure water at 62° F., is the specific gravity required.

Fig. 564.



This hydrometer would admit of more accurate results than the common instrument, but would be inconvenient in common use.

Nicholson's *Hydrometer* (*fig.* 564), invented by the author of the "Chemical Dictionary," is an ingenious modification of Fahrenheit's hydrometer, by which it is rendered capable of determining specific gravities of solid bodies as well as of liquids. It has a single mark on the stem, and bears three scale-pans, one at the summit of the stem, above the surface of the liquid, and the other two, one of which is concave downwards, at the lower extremity of the instrument. When it is placed in water, the air must be allowed to escape from this lowest scale-pan.

In taking the specific gravities of liquids, this hydrometer is identical with that of Fahrenheit. The weight of the instrument is generally adjusted from the first so that 1,000 grains placed in the upper dish will cause it to sink in pure water, at 62° F., up to the mark on the stem. Let the weight, however, required for this purpose, whatever it may amount to, be called w_1, the weight of the instrument itself being W. When placed in a liquid of which the specific gravity differs from that of water, and is required to be known, a weight w_2 less or greater than w must be placed in the upper pan to sink it to the zero mark. Then $\frac{W + w_2}{W + w_1}$ is obviously the specific gravity required.

To take the specific gravity of any solid substance, a portion of it weighing less than w_1 is placed in the upper pan, with such additional weight, say w_3, that the hydrometer will sink in pure water up to the zero mark, as it does when loaded with w_1.

Then the weight of the substance is obviously $w_1 - w_3$. Now transfer the substance to one of the lower pans, that which is concave downwards being used when the substance is lighter than water, and has to be forced under. The instrument must again be adjusted so as to float in water at the usual level, and it will be found that some further weight has to be added for this purpose. Let the weight now in the pans be w_4. Then the specific gravity of the substance is $\frac{w_1 - w_3}{w_4 - w_3}$.

This instrument becomes more and more delicate and accurate in its indications as the stem is of smaller diameter. As actually constructed by the inventor, the stem was a piece of hardened steel wire $\frac{1}{40}$ inch in diameter. But the more delicate, the more troublesome does the instrument become in use; the adherence of water to the parts above the surface, the adherence of air to those below, and the inevitable changes of temperature in the water, are sources of unavoidable error. The chemist, in his balance and specific gravity bottle, has always at hand the means of ascertaining specific gravities with any degree of accuracy, and is not likely to use Nicholson's hydrometer. But this instrument is a valuable companion to the scientific traveller; since, besides its use in taking specific gravities, it may be employed in place of a balance for ascertaining any small weight.

Having now given all that it is likely to be practically useful concerning the hydrometer, we think it quite needless to describe all the minute varieties of construction and arbitrary scales proposed by Homberg, Clarke, Gay-Lussac, Dica, Richter, Adie, Quin, Guyton, Speers, Charles, and others. Much information is given in the *Handwörterbuch der Chemie*, 2te Aufl., &c., ii. 165-190.

The hydrometer is said to have been first invented by Hypatia, daughter of Theon Alexandrinus, who flourished about the end of the fourth century, but the discovery is sometimes ascribed to Archimedes. However this may be, the English philosopher Robert Boyle appears to have first brought it into use, having described it in Phil. Trans. for 1675 (x. 329), or *Boyle's works* (1772, iv. 204). His instrument was almost identical with Nicholson's hydrometer, and was especially intended to determine the fineness of gold alloys, being hence called a "*New Essay Instrument.*"

Many references concerning the history and varieties of the hydrometer will be found in *Young's Lectures* [1845] i. 240.—*Bénoit's Théorie Générale des Pèse-liqueurs* [1821], is a work we have not been able to meet with. Clarke's hydrometer (Phil. Trans. xxxvi. [1730], p. 277), Brewster's Capillary Hydrometer, Staktometer, or Drop-measurer, are described in the Edinburgh Cyclopædia, xi. pt. ii. p. 442.—W. S. J.

HYDRONICKELMAGNESITE, also called *Pennite.* A variety of hydrodolomite (p. 191) containing 2 per cent. or less of carbonate of nickel, with water. It forms pale-green or whitish incrustations, having a surface of minute spherules, and occurs together with emerald-nickel, into which it graduates, also with chromic iron, at Texas, Lancaster county, Pennsylvania, and according to Heddle, at Swinaness, in Unst, Shetland. Hermann found in it 44·54 CO^2, 20·10 Ca^2O, 27·02 Mg^2O, 1·25 Na^2O, 0·70 Fe^2O, 0·40 Mn^2O, 0·15 Al^4O^3, and 5·84 H^2O = 100. (Dana, ii. 457.)

HYDROPHANE. A variety of opal, which becomes transparent when immersed in water.

HYDROPHILITE. A name applied to chloride of calcium.

HYDROPHITE, also called *Jenkinsite.* A hydrated silicate of magnesium and iron, which occurs massive, and sometimes fibrous. Specific gravity 2·46–2·65. Hardness = 3·5. Lustre, feeble, subvitreous. Colour, mountain-green to blackish-green: streak pale; translucent to opaque.

	SiO^2	Fe^2O	Mn^2O	Mg^2O	Al^4O^3	V^2O^3	H^2O.	
a.	36·19	22·73	1·66	21·08	2·895	0·125	16·08	= 100·75
b.	38·97	19·30	4·36	22·87	0·53	. .	13·36	= 99·38
c.	37·42	20·60	4·05	22·75	0·98	. .	13·46	= 99·28

a. Hydrophite from Taberg, in Sweden (Svanberg, Pogg. Ann. li. 535).—*b. Jenkinsite* from O'Neil's mine, Orange county, New York (Smith and Brush, Sill. Ann. J. ii. 369). These analyses lead to the formula $\left.\begin{matrix}\frac{3}{5}Mg^2O\\ \frac{2}{5}Fe^2O\end{matrix}\right\}^4.3SiO^2.3H^2O$; which regarding 2 at. water as basic, may be reduced to the form of an orthosilicate, $3(2M^2O.SiO^2).H^2O$, or $3M^4SiO^4.H^2O$.

HYDROPITE. A silicate of manganese with excess of manganous oxide, containing, according to Du Menil's analysis, 54·37 per cent. SiO^2, 41·33 Mn^2O, 0·92 Fe^2O, and 1·25 Ca^2O. (*Rammelsberg's Mineralchemie*, p. 459.)

HYDROPSIN. The name given by Garnal (Schmidt's Jahrb. d. ges. Méd. cvi. 8) to an albuminous substance which he obtained from a dropsical effusion.

HYDROQUINONE. *Hydrochinone, Hydrokinone* (Wöhler, Ann. Ch. Pharm. xlv. 354; li. 150; Hesse, *ibid.* cx. 194; cxiv. 292).—This name is applied to two substances, one colourless and the other green.

COLOURLESS HYDROQUINONE (*Pyroquinole*), $C^6H^6O^2$, isomeric with oxyphenic acid, is the chief product of the dry distillation of quinic, carbohydroquinonic, and oxysalicylic acids (*q. v.*), and is likewise produced by the action of reducing agents (stannous chloride or sulphurous acid) on quinone, from which it differs by 2 at. H; also, together with a brown crystalline body containing $C^{18}H^{14}N^2O^2$, by the action of phenylamine on quinone (A. W. Hofmann, Proc. Roy. Soc. xiii. 4):

$$\underset{\text{Phenylamine.}}{2C^6H^7N} + \underset{\text{Quinone.}}{3C^6H^4O^2} = \underset{\text{Brown crystals.}}{C^{18}H^{14}N^2O^2} + \underset{\text{Hydroquinone.}}{2C^6H^6O^2}.$$

Preparation.—1. The distillate, mixed with solid particles, which is obtained by the dry distillation of quinic acid, is filtered from tar, and again, after cooling, to separate benzoic acid; the yellow, heavy, oily mixture of benzene, phenic acid and salicylous acid, is distilled from the filtrate; the brown residue in the retort is evaporated and left to cool till benzoic acid crystallises out; the mother-liquor is diluted with water, which makes the liquid milky and separates tar; and the resulting filtrate is evaporated till the hydroquinone crystallises out.—2. Sulphurous acid gas is passed through warm water saturated with quinone, and having quinone also suspended in it, till all the quinone is dissolved, and the liquid appears colourless; the solution is then gently evaporated to the crystallising point, and the crystals are purified by pressure and recrystallisation.—It is not necessary previously to remove the sulphuric acid by carbonate of barium.—A saturated aqueous solution of quinone may also be mixed with aqueous hydriodic acid, and the watery liquid, after filtration from the iodine, evaporated to the crystallising point.

Properties.—Hydroquinone forms transparent, colourless, rhombic crystals exhibiting the combination, $\infty\bar{P}\infty \,.\, \infty\breve{P}\infty \,.\, P \,.\, oP$ (Hesse). It sublimes, when heated, in shining laminæ, like benzoic acid; melts at 177·5° and solidifies to a crystalline mass at 163°. It is inodorous, has a sweetish taste, and is neutral to vegetable colours. It dissolves easily in *water*, especially when hot, also in *alcohol* and in *ether*. From solutions of *alkaline sulphites*, it crystallises unaltered, sometimes however in sulphur-yellow rhombohedrons or long four-sided prisms, resembling the sulphydrates of hydroquinone. (Hesse.)

Decompositions.—1. Hydroquinone, suddenly heated above the boiling point, is partially decomposed into quinone and green hydroquinone. When passed in the state of vapour through a glass tube at a low red heat, it is resolved into quinone and hydrogen (Hesse).—2. *Oxidising agents*, viz. chlorine, chromate of potassium, sesquichloride of iron, or nitrate of silver, convert hydroquinone dissolved in water into green hydroquinone, with formation of hydrochloric acid, chromic oxide, or protochloride of iron and hydrochloric acid, or with precipitation of silver.—3. Strong *nitric acid* converts it almost wholly into oxalic acid (Hesse).—With *hydrochloric acid and chlorate of potassium* it yields tetrachlorquinone (chloranil) (Hesse).—4. The aqueous solution of hydroquinone imparts a saffron-yellow colour to *cupric acetate*, and when heated throws down cuprous oxide, quinone volatilising at the same time.—5. *Ammonia* imparts to it a brown-red colour, and yields on evaporation a brown mass like ulmic acid. *Potash* acts in like manner. (Wöhler.)

Hydroquinone dissolves in a moderately concentrated hot solution of neutral *acetate of lead*, and the solution, on cooling, yields prisms containing $C^6H^6O^2.2C^2H^3PbO^2 + \frac{3}{2} H^2O$. These crystals give off 5·23 per cent. of water (nearly $\frac{3}{2}$ at.) over sulphuric acid.

Sulphydrates of Hydroquinone.—There are two of these salts. The first, containing $4C^6H^6O^2.H^2S$, is obtained in colourless prisms by passing sulphydric acid gas into a saturated solution of hydroquinone heated to 40°.—The second $3C^6H^6O^2.H^2S$, is obtained, by passing sulphydric acid into a cold saturated solution of hydroquinone, in small shining crystals, which redissolve when heated if the passage of the gas be continued, the solution, as it cools, yielding the compound in very regular colourless rhombohedrons. These crystals remain unaltered when dry, but water eliminates sulphydric acid from them, and on boiling the solution, hydroquinone is reproduced.

GREEN HYDROQUINONE OR QUINHYDRONE. $C^{12}H^{10}O^4 = C^6H^6O^2.C^6H^4O^2$.—This compound may be regarded either as a compound of quinone and colourless hydroquinone, or as a double molecule of the latter compound *minus* 2 at. H, or again as a double molecule of quinone ($C^{12}H^8O^4$) *plus* 2 at. H.

It is produced:—1. By mixing the aqueous solutions of quinone and hydroquinone, whereupon it is immediately precipitated in the crystalline form.—2. By combining aqueous quinone with a quantity of hydrogen not sufficient for the formation of colourless hydroquinone; *e. g.* aqueous quinone mixed with sulphuric acid at the negative pole of the galvanic circuit; quinone mixed with sulphuric acid in contact with zinc; aqueous solution of quinone with gradual addition of dichloride of tin or protosulphate of iron, or sulphurous acid, or alloxantin, the latter being converted into alloxan.—3. By the partial dehydrogenation of aqueous hydroquinone; *e.g.* when spongy platinum or animal charcoal moistened with the solution is exposed to the air; when chlorine gas is passed through aqueous hydroquinone, or that liquid is mixed with nitric acid, chromate of potassium, sesquichloride of iron, or nitrate of silver.—The mixtures prepared according to (2) or (3) with concentrated solutions, assume for a while a black-red colour, and then become filled with long, green, metallic-looking prisms of quinhydrone; but if the solutions are too dilute, the quinhydrone remains dissolved and is decomposed, emitting the odour of quinone.—The largest crystals are obtained by at once adding to a saturated aqueous solution of quinone (or even to its mother-liquor) a quantity of aqueous sulphurous acid just half sufficient for the formation of hydroquinone.

Properties.—Quinhydrone forms very long and thin green prisms, having a metallic lustre, like the wings of gold-beetles or humming birds, and brighter even than murexid; they appear red-brown by transmitted light when strongly magnified. It melts easily to a brown liquid, and sublimes partly undecomposed in green laminæ. Smells slightly like quinone, and has a pungent taste.

It dissolves sparingly in cold *water*, abundantly and with red-brown colour in hot water, separating as it cools. *Alcohol* and *ether* dissolve it readily, forming yellow or red solutions. *Ammonia* dissolves it with green colour. The aqueous solution forms with *acetate of lead* a bright greenish-yellow precipitate, quickly changing to dirty grey.

Decompositions.—1. When quinhydrone is heated, it sublimes partly undecomposed, partly converted into yellow quinone.—2. When it is boiled with water, quinone distils over, and the remaining dark red-brown liquid contains, together with a large quantity of hydroquinone, a brown tar, which separates partly on cooling, partly on subsequent addition of water.—3. The green solution of quinhydrone in *ammonia* quickly assumes a dark red-brown colour on exposure to the air, and leaves a brown amorphous mass when evaporated.—4. Quinhydrone is converted into colourless hydroquinone by aqueous *sulphurous acid*, *stannous chloride*, or *zinc and sulphuric acid*, but not by hydriodic acid or tellurhydric acid.—5. The aqueous solution quickly reduces *nitrate of silver*, on addition of ammonia.

Derivatives of Hydroquinone.

Carbohydroquinonic acid. $C^7H^6O^4 = C^6H^6O^2.CO^2 = \left.\begin{matrix}(C^7H^3O)'''\\ H^3\end{matrix}\right\}O^3$. (O. Hesse, Ann. Ch. Pharm. cxii. 527, cxiv. 292; cxxii. 22; E. Lautemann, *ibid.* cxx. 315).—An acid produced:—1. By the action of bromine on aqueous quinic acid.—2. By heating quinic acid to above 200°.—3. Small quantities of it are likewise obtained by the action of chlorate of potassium and hydrochloric acid on dilute aqueous quinic acid, or of peroxide of manganese and sulphuric acid on aqueous quinate of calcium. (Hesse.)

Preparation.—Bromine is added to aqueous quinic acid by portions of 10 drops each, till a portion of it remains undissolved, even after the liquid has been frequently agitated and left to stand for 12 hours. The solution is then decanted from the undissolved bromine, diluted, filtered, and mixed with carbonate of lead, as long as a brisk evolution of gas is thereby set up, and bromide of lead produced. The filtrate, evaporated to a thick syrup on the water-bath, and shaken up with about 5 vol. ether, yields to this liquid carbohydroquinonic acid, which after the ether has been distilled off, remains as a brown crystalline residue. It is purified by re-crystallisation from water containing hydrochloric acid, with help of animal charcoal.—Or the solution, treated with bromine and filtered, is mixed with carbonate of lead, till this salt begins to take up organic substances; the filtrate is precipitated with solution of neutral acetate of lead, and then, after this precipitate has been collected, a further precipitate is obtained by addition of ammonia. By decomposing the precipitates suspended in water with sulphydric acid, then boiling up and diluting the filtrate, carbohydroquinonic acid is obtained from the first precipitate. The acid obtained from the second lead-precipitate still retains unaltered quinic acid, from which it may be separated by ether. (Hesse.)

Properties.—Carbohydroquinonic acid crystallises from its aqueous solution with 1 at. water ($C^7H^6O^4.H^2O$), in furcate groups of needles, also in rhombic laminæ or granular crystals. It is dimorphous. The granular crystals are distorted twins, belonging to the monoclinic system. The needles are rhombic prisms, having the acute edges perpendicularly truncated, cleavable at right angles to the prismatic faces (Hesse).—The crystallised acid dissolves in 40 or 50 pts. of *water* at 17°, very easily in boiling water and in *alcohol*, but is insoluble in *ether*. It has a sour and bitter taste and reddens litmus. Heated to 100° it gives off, on the average, 10·5 per cent. water, leaving the anhydrous acid, $C^7H^6O^4$, which melts at 207° (corrected) with partial decomposition, and solidifies in the radio-crystalline form between 160° and 170° (Hesse). When cautiously heated, it sublimes with partial decomposition. (Lautemann.)

Decompositions.—1. Carbohydroquinonic acid is resolved by fusion, and with great facility when heated to 240°, into carbonic anhydride and hydroquinone, $C^7H^6O^4 = C^6H^6O^2 + CO^2$ (Hesse). When it is heated with pumice, pyrocatechin is obtained instead of hydroquinone, the former being apparently capable of passing, under circumstances not exactly known, into hydroquinone (Lautemann).—2. It is not altered by boiling dilute *nitric acid;* the concentrated acid converts it, with rise of temperature and evolution of nitrous acid, into oxalic acid, together with a trace of a yellow substance.—3. *Sulphuric anhydride* dissolves it, without evolution of gas, forming a blue liquid, brownish by reflected light. No conjugated sulphuric acid can be obtained from this solution.—In *oil of vitriol*, carbohydroquinonic acid dissolves slowly, and chars when heated.—4. *Bromine* dissolves slowly in the aqueous acid, with evolution of gas.—5. Aqueous carbohydroquinonic acid, in contact with *acid carbonate of calcium* and air, acquires a dark, nearly black colour, and deposits a black precipitate, which effervesces with acids (Hesse).—6. From *cupric hydrate* and *potassio-cupric tartrate* aqueous carbohydroquinonic acid separates cuprous oxide; from *mercuric* and *silver-salts* it separates the metal. Dilute aqueous carbohydroquinonic acid, mixed at 8° or 10° with neutral solution of *nitrate of silver*, becomes dark-coloured in a quarter of an hour, even in the dark, and in three hours separates metallic silver (Hesse). According to Lautemann it reduces nitrate of silver when heated, but not in the cold.

The carbohydroquinonates are, for the most part, easily soluble in water, sparingly soluble or insoluble in alcohol. Hesse regards the acid as monobasic, and the ammonium-salt as a basic salt, in which 1 at. ammonia takes the place of water of crystallisation, $C^7H^5(NH^4)O^4.NH^3$. The formula $\left.\begin{matrix}(C^7H^3O)'''\\H^3\end{matrix}\right\}O^3$ represents it as triatomic but monobasic, like glyceric acid (ii. 875). Strecker (*Handwörterb.* ii. [2], 996), regards the acid as dibasic. Carbohydroquinonic acid decomposes the carbonates of the alkaline earths. Its salts turn brown in the air. In contact with a small quantity of sesquichloride of iron, they acquire a violet colour; with a larger quantity, a fine purple-violet to chrome-green colour especially in neutral solution. (Hesse.)

Ammonium-salts.—When dry ammonia-gas is passed over dry carbohydroquinonic acid, 100 pts. of the acid take up from 22·3 to 22·7 pts. of ammonia (2 at. = 22·08 NH^3), without giving off water. The resulting compound, freed from excess of ammonia by standing over oil of vitriol, contains 44·7 per cent. C, and 6·2 H, corresponding to the formula, $C^7H^5(NH^4)O^4.NH^3$ (calc. 44·68 per cent. C, and 6·38 H). When exposed to moist air, it quickly gives off ammonia, and dissolves, with alkaline reaction, in water and alcohol. The latter solution, when evaporated, deposits small acid crystals. Hydrated ether partially dissolves the ammonium-salt, leaving a portion, perhaps consisting of $C^7H^5(NH^4)O^4.H^2O$. An ether-alcoholic solution of carbohydroquinonic acid becomes turbid when ammonia gas is passed over it, and then clear, depositing concentric groups of prisms. Brown substances are formed at the same time. (Hesse.)

Lead-salt.—From aqueous carbohydroquinonic acid, an aqueous or alcoholic solution of neutral acetate of lead throws down an amorphous yellow precipitate, easily soluble in nitric acid, with difficulty in acetic acid. Part of the carbohydroquinonic acid dissolves at the same time in the acetic acid which is set free, so that the filtrate still gives a precipitate with ammonia. (Hesse.)

The *potassium-salt* is precipitated from its aqueous solution by alcohol in the form of a syrup.—The *manganous salt* forms small prisms, easily soluble in water.—The *zinc-salt* forms laminæ.—Aqueous carbohydroquinonic acid yields a greyish-yellow precipitate with *tartar emetic*; and with *ferric hydrochlorate*, a dark green solution changing to violet on addition of acid carbonate of sodium, or of tartaric acid, ferric hydrochlorate, and ammonia. It does not precipitate *gelatin*.

The following acids give reactions very similar to those of carbohydroquinonic acid: 1. *Morintannic acid* and *Morin*, which, according to Hlasiwetz, are isomeric with carbohydroquinonic acid.—2. *Deuterocatechuic acid*, $C^8H^8O^4$, and *Tricatechuic acid*, $C^9H^{10}O^4$. These two acids are supposed by Strecker (Ann. Ch. Pharm. cxviii. 280) to exist in catechu, inasmuch as he regarded the pyrocatechin, first as the one, then as the other of these acids, and finally, as a mixture of the two.—3. *Protocatechuic acid.* This acid, according to Lautemann (Ann. Ch. Pharm. cxx. 315), must be regarded as identical with carbohydroquinonic acid, since the latter acid, when heated with pumice, is capable of yielding pyrocatechin. But according to Hesse (Ann. Ch. Pharm. cxxii. 221), the two acids react differently with cupric tartrate, and must therefore be regarded as only isomeric.—4. *Oxysalicylic acid.* With regard to this acid, Lautemann thinks it probable that it may be capable of passing into carbohydroquinonic acid (or the latter into oxysalicylic acid).—5. *Hypogallic acid.*

Ethyl-carbohydroquinonic acid, $C^9H^{10}O^4 = \left.\begin{matrix}(C^7H^3O)'''\\ H^2.C^2H^5\end{matrix}\right\}O^3$. *Carbohydroquinonic ether.*—To prepare this compound, carbohydroquinonic acid is dissolved in alcohol of 90 per cent.; the solution is saturated with hydrochloric acid gas; the alcohol is distilled off in the water-bath; the residue is shaken up with ether, as long as that liquid takes up a substance which colours ferric chloride; the ether is then distilled off; the brown crystalline residue is shaken up with boiling, very dilute alcohol, and a small quantity of carbonate of sodium; the solution is left to cool; and the acid is again exhausted with ether. The ethereal solution when evaporated leaves coloured crystals, which may be decolorised by again treating them with dilute alcohol, soda, and ether. It forms colourless prisms united in radiate groups, neutral, melting at 134° (corrected), and becoming crystalline again at 124·3°.

The ether melts in boiling water before dissolving; dissolves easily in *alcohol*, and especially in common *ether*. The aqueous solution, added to *neutral acetate of lead*, forms a white amorphous precipitate soluble in acetic acid; it colours *ferric hydrochlorate* violet, changing to purple-violet on addition of a larger quantity of the iron-salt, and finally to chrome-green. It reduces *mercuric chloride*, *nitrate of silver*, and *potassio-cupric tartrate.* (Hesse, *loc. cit.*)

Chlorinated Hydroquinones. (Wöhler, Ann. Ch. Pharm. li. 155.—Städeler, *ibid.* lxix. 132, 306, 321.)—These compounds are produced by the action of reducing agents on the corresponding chlorinated derivatives of quinone: they are most easily prepared by means of sulphurous acid. They bear a greater resemblance to hydroquinone in proportion as they contain less chlorine. They act like weak acids, their alcoholic solutions yielding white precipitates with acetate of lead, the quantity of the precipitate being increased by addition of ammonia. The chlorine in these compounds does not exhibit its usual reaction with nitrate of silver. By oxidising agents, viz. by nitric acid and sesquichloride of iron, they are converted either into the corresponding chlorinated quinones, or compounds of these with the chlorinated hydroquinones.

Monochlorinated Hydroquinone, $C^6H^5ClO^2$, forms tufts of colourless prisms, very soluble in water, alcohol and ether, and liquefying in contact with the vapour of ether. It melts easily, and sublimes in white laminæ, with partial decomposition. Its aqueous solution reduces nitrate of silver. It dissolves in ammonia, forming a dark-blue solution, changing to green, yellow, and red-brown.

Dichlorinated Hydroquinone, $C^6H^4Cl^2O^2$, forms beautiful nacreous crystals, which melt at 164°, and begin to sublime at 120°. It reddens litmus; dissolves sparingly in cold water, easily in boiling water, also in alcohol, in ether, and in hot acetic acid; sparingly in boiling hydrochloric acid; it is soluble also in hot concentrated sulphuric acid, and separates on cooling. With dilute potash it forms a colourless solution, which on exposure to the air turns green, then red, and deposits a violet powder. With ammonia, it forms a yellow solution, which reddens in contact with the air, and deposits a brownish precipitate.

Trichlorinated Hydroquinone, $C^6H^3Cl^3O^2$, forms colourless laminæ, or flattened prisms melting at a little above 130°, and subliming in iridescent scales. It dissolves readily in alcohol and in ether; the alcoholic solution reddens litmus. It dissolves in potash and in ammonia, forming green solutions, which turn first red, then brown, and yield copious precipitates with hydrochloric acid.

Tetrachlorinated Hydroquinone, $C^6H^2Cl^4O^2$, forms colourless, nacreous laminæ, insoluble in water, very soluble in alcohol and ether; its solutions redden litmus. When heated, it begins to turn brown at 160°, the colour becoming stronger towards 220°; it then sublimes rapidly, but does not melt till more strongly heated; the melted mass crystallises on cooling. It dissolves in potash and in ammonia. The potash solution, saturated hot, deposits on cooling, prismatic crystals, apparently consisting of a potassium-salt.

Octochlorinated Acetyl-dihydroquinone, $C^{14}H^6Cl^8O^5 = C^{12}H^3(C^2H^3O)Cl^8O^4$ (Hesse, Ann. Ch. Pharm. cxiv. 292).—Produced by passing sulphurous anhydride into a mixture of tetrachloroquinone and glacial acetic acid, then evaporating and subliming:

$$2C^6Cl^4O^2 + C^2H^4O^2 + H^2O + 2SO^2 = C^{14}H^6Cl^8O^5 + 2SO^3.$$

It forms colourless laminæ, which melt at 230°, dissolve easily in ether, alcohol, hot benzene, and strong acetic acid, but are nearly insoluble in water.

Octochlorinated Ethyl-dihydroquinone, $C^{14}H^8Cl^8O^4 = C^{12}H^3(C^2H^5)Cl^8O^4$ (Hesse, *loc. cit.*).—Obtained by passing sulphurous anhydride for some time through a heated mixture of tetrachloroquinone with 20 pts. alcohol of 92 per cent. The tetrachloroquinone then dissolves, and the solution mixed with water yields the octochlorinated ethylhydroquinone, which crystallises from benzene in colourless rhombic laminæ, often an inch long, and exhibiting the combination $\infty\breve{P}\infty \,.\, \infty P \,.\, m\breve{P}\infty$. The compound melts at 236°, sublimes almost unaltered at 210°; is nearly insoluble in water and in solutions of sulphites, but dissolves easily in alcohol, ether, hot benzene, and acetic acid. The alcoholic solution after a while becomes acid and brown-coloured, and ultimately deposits black prisms having a metallic lustre; on addition of hypochlorite of sodium, the solution yields green crystals, and then tetrachloroquinone. Octochlorinated ethylhydroquinone mixed with quicklime, and moistened with a few drops of water, exhibits a fine green colour.

Chlorinated Quinhydrones.—The chlorinated hydroquinones combine with the chlorinated quinones, forming compounds which may be regarded as chlorinated quinhydrones (p. 213). These compounds are produced by mixing the aqueous solutions of their components, or by the action of oxidising agents on the chlorinated hydroquinones, or of reducing agents on the chlorinated quinones. The *dichlorinated* compound, $C^6H^5ClO^2.C^6H^3ClO^2$, sublimes in brown needles, which colour the skin purple, and redden litmus.—The *tetrachlorinated* compound, $C^6H^4Cl^2O^2.C^6H^2Cl^2O^2$, in the anhydrous state, forms yellow crystals; in the hydrated state, with $2H^2O$, it forms violet crystals.—The *hexchlorinated* compound, $C^6H^3Cl^3O^2.C^6HCl^3O^2$, appears to be formed by treating trichloroquinone with a quantity of sulphurous acid not sufficient to convert it completely into trichlorinated hydroquinone; and the *octochlorinated* compound, $C^6H^2Cl^4O^2.C^6Cl^4O^2$, by the action of nitrate of silver on perchlorinated hydroquinone.

Phosphohydroquinonic acid. $C^6H^7PO^5 = C^6H^6O^2.PHO^3$ (Hesse, Ann. Ch. Pharm. cxiv. 292).—Quinic acid dissolves in cold dilute aqueous phosphoric acid without decomposition; but on evaporating the solution, a copious evolution of gas takes place at a certain degree of concentration, and the remaining brown solution contains an acid, whose calcium-salt, which separates partly crystalline, partly amorphous, has the composition $C^6H^5CaPO^5$. The formation of the acid is represented by the equation:

$$\underset{\text{Quinic acid.}}{C^7H^{12}O^6} + PH^3O^4 = \underset{\substack{\text{Phosphohydro-}\\\text{quinonic}\\\text{acid.}}}{C^6H^7PO^5} + CO + 4H^2O.$$

Sulphite of Hydroquinone. $C^{18}H^{18}SO^8 = 3C^6H^6O^2.SO^2$ (A. Clemm, Ann. Ch. Pharm. cx. 345).—When sulphurous anhydride is passed through a solution of quinone till that compound is completely converted into colourless hydroquinone, and the passage of the gas is then further continued, the liquid again turns yellow, and deposits, after concentration, yellow rhombohedral crystals having the above composition. This compound is very easily decomposible, and gives off sulphurous anhydride when heated, leaving colourless hydroquinone.

Sulphohydroquinonic acids. Acids containing the elements of hydroquinone and sulphuric anhydride; produced by the action of sulphuric acid or anhydride on quinic acid and hydroquinone. (O. Hesse, Ann. Ch. Pharm. cx. 194; cxiv. 292.)

1. *Disulpho-hydroquinonic acid*, $C^6H^6S^2O^8 = C^6H^6O^2.2SO^3$.—*Preparation of the barium-salt.*—Fuming sulphuric acid is poured into fused or finely pulverised quinic acid, till a fresh addition no longer causes any considerable evolution of gas; the liquid is gently warmed towards the end of the operation, diluted after cooling with a large quantity of water, neutralised with carbonate of barium, and evaporated to the crystallising point. The crystals which first separate take up a large quantity of colouring matter, so that the mother-liquor yields a less coloured salt.

The aqueous acid, obtained by decomposing the barium-salt with the exactly equivalent quantity of sulphuric acid, or the lead-salt with sulphydric acid, forms an acid syrup, easily soluble in *alcohol*, insoluble in *ether*.

The acid is *dibasic*, but only the dimetallic salts have been obtained. The salts and the aqueous acid produce with ferric hydrochlorate a fine blue colour, which disappears on heating, and reappears with a dingy tint on cooling. The blue colour is also destroyed, slowly by access of air, or by addition of nitric or acetic acid, quickly by addition of hydrochloric, sulphuric, or tartaric acid. A similar action is exerted by sal-ammoniac, chloride of barium, chloride of calcium, sulphate of magnesium, phosphate of sodium, neutral acetate of lead, and ferric hydrochlorate. The salts separate metallic silver from the nitrate.

The *ammonium-salt*, obtained by decomposing the barium-salt with carbonate of ammonia, separates from the concentrated solution in large crystals.

The *barium-salt*, $C^6H^4Ba^2S^2O^8.4H^2O$, forms beautiful monoclinic prisms, with angles of 113° 4′. When heated, it gives off suffocating vapours, hydroquinone, quinhydrone, and water, leaving a residue of charcoal. The salt dried in the air, or over oil of vitriol, gives off at 90° from 10·8 to 11·5 per cent. water (3 at. = 11·31 per cent. H^2O), then between 120° and 160° an additional 3·3 per cent. (1 at. = 3·77 per cent. H^2O), corresponding in all to 4 at. The salt dissolves readily in boiling water, with difficulty in cold water, and in alcohol either cold or boiling, but is insoluble in ether.

The *calcium-salt* resembles the barium-salt.

The *lead-salt*, $C^6H^4Pb^2S^2O^8.2PbHO$, is separated from the concentrated solution of the barium-salt by neutral acetate of lead, as a bulky precipitate, which quickly changes into yellowish microscopic crystals having a silky lustre. When heated, it assumes a lemon-yellow colour, and becomes carbonised. It is nearly insoluble in water and acetic acid, easily soluble in nitric acid, precipitable by ammonia.

The *potassium-salt*, $2C^6H^4K^2S^2O^8.3H^2O$, is obtained by neutralising the aqueous acid with carbonate of potassium, and separates with the same composition, even from solutions containing 2 at. acid to 1 at. potash. It forms colourless prisms having a saline taste, easily soluble in water, sparingly in alcohol. They retain 6·9 per cent. water over oil of vitriol, give off the whole at 150°, and decompose when melted.

2. *Sulphodihydroquinonic acid*, $C^{12}H^{16}SO^9 = 2C^6H^6O^2.SO^3.2H^2O$.—Produced by the action of fuming sulphuric acid on hydroquinone. The solution, which is formed without evolution of gas, yields, when saturated with carbonate of barium, a barium-salt, which crystallises in concentrically grouped needles containing $C^{12}H^{15}BaSO^9$. This salt is easily soluble in water and in aqueous alcohol, sparingly soluble in absolute alcohol, and is precipitated therefrom in flocks by ether.

3. *Disulphodihydroquinonic acid*, $C^{12}H^{14}S^2O^{11} = 2C^6H^6O^2.2SO^3.H^2O$.—Hydroquinone exposed to the vapour of sulphuric anhydride deliquesces and yields this acid. The *potassium-salt*, $C^{12}H^{13}KS^2O^{11}$, crystallises in colourless monoclinic prisms or in flattened, sharp-pointed needles, easily soluble in water and in hot alcohol. The solution treated with ferric hydrochlorate acquires a transient dark-blue colour; it forms a white precipitate with ammoniacal acetate of lead, and reduces silver from the nitrate.

HYDROSALICYLAMIDE. $C^{21}H^{18}N^2O^3 = N^2(C^7\overset{''}{H^6}O)^3$. *Salhydramide. Salicylimide. Hydride of Azosalicyl* (Ettling, Ann. Ch. Pharm. xxxv. 261).—This compound is produced by the action of ammonia on hydride of salicyl (salicylous acid):

$$3C^7H^6O^2 + 2NH^3 = C^{21}H^{18}N^2O^3 + 3H^2O.$$

The hydride of salicyl is dissolved in 3 or 4 times its volume of cold alcohol, and a quantity of ammonia is added equal to that of the hydride of salicyl employed. The solution then immediately yields yellowish-white needles, and soon solidifies in a mass. On applying a gentle heat, the product dissolves completely, and the liquid, on cooling, deposits crystals of hydrosalicylamide.

Hydrosalicylamide crystallises in triclinic prisms, without modification. Angle $\infty{,}P : \infty P{,}' = 117° 30'$; $oP : \infty{,}P = 103° 30'$; $oP : \infty P{,}' = 93° 30'$. It appears to be insoluble in *water*, and dissolves but sparingly in cold *alcohol*, but quickly in about 50 pts. of boiling alcohol. At 300° it melts to a yellow and brownish mass, yielding a white, very light sublimate. At a higher temperature it carbonises. It is not decomposed by weak *potash-ley* in the cold, but on boiling it gives off ammonia and forms salicylide of potassium. Dilute *acids* also do not decompose it in the cold, but on heating, ammonia is produced, and hydride of salicyl is set free. With an alcoholic solution of *sulphydric acid*, it yields hydride of sulphosalicyl:

$$\underset{\text{Hydrosalicyl-amide.}}{C^{21}H^{18}N^2O^3} + 3H^2S = \underset{\text{Hydride of sulpho-salicyl.}}{3C^7H^6OS} + 2NH^3.$$

Hydrosalicylamide forms several salts in which part of the hydrogen is replaced by metallic radicles.

The *cupro-cuprammonic salt*, $C^{21}H^{15}Cu^2(NH^3Cu)N^2O^3$, is obtained by mixing a very dilute and slightly cooled alcoholic solution of hydrosalicylamide with ammoniacal acetate of copper (acetate of cuprammonium). The liquid immediately acquires a fine emerald-green colour, and gradually deposits brilliant laminæ of the same colour, the solution being at the same time decolorised. The crystals are insoluble in water and in alcohol; they dissolve in cold dilute acids, but are reprecipitated on saturating the solution with an alkali. Strong mineral acids decompose them completely, liberating hydride of salicyl. Dilute potash does not decompose them without the aid of heat, and even then but slowly. They melt when heated, and yield by distillation an oil which solidifies on cooling, in a crystalline mass having the odour of gum-benzoin.

Ferrico-ferricammonic salt, $C^{21}H^{15}\mathit{fe}^2(NH^3\mathit{fe})N^2O^3$.—To prepare this salt, an aqueous solution of ferric chloride is mixed with a quantity of tartaric acid sufficient to prevent its precipitation by a large excess of ammonia; a saturated alcoholic solution of hydrosalicylamide is then mixed with a quantity of ammonia sufficient to enable it to be treated with 30 or 40 times its volume of cold water without becoming turbid; and the two solutions are mixed. The mixture immediately acquires a deep blood-red colour, and after some time deposits a yellowish-red flocculent precipitate which gradually becomes darker coloured and granular. This precipitate is partially soluble in alcohol. It is not decomposed by cold dilute hydrochloric acid, but the hot concentrated acid decomposes it, with separation of hydride of salicyl.

Lead-salts.—Two of these salts appear to exist. One of them is obtained by mixing a solution of acetate of lead with ten times its volume of alcohol, heating the mixture, pouring in a little ammonia, and adding an alcoholic solution of hydrosalicylamide containing a small quantity of ammonia till the precipitate which forms at first no longer redissolves in the hot liquid; this liquid on cooling deposits a yellow granular powder.—The other lead-salt of hydrosalicylamide is obtained by mixing a solution of the hydramide with aqueous ammonia, and adding in the cold a solution of acetate of lead. Light yellow flocks are then formed, which become strongly electric by friction.

Hydrobromosalicylamide. $C^{21}H^{15}Br^3N^2O^3 = N^2(C^7\overset{\prime\prime}{H}{}^4BrO)^3$. *Hydride of Bromazosalicyl. Bromosamide.*—Obtained by the action of ammonia on hydride of bromosalicyl (bromosalicylous acid). Its properties and reactions are precisely analogous to those of the following compound. (Piria.)

Hydrochlorosalicylamide. $C^{21}H^{15}Cl^3N^2O^3 = N^2(C^7\overset{\prime\prime}{H}{}^4ClO)^3$. *Hydride of Chlorazosalicyl. Chlorosamide* (Piria, Ann. Ch. Phys. [2] lxix. 309).—Produced by the action of ammonia-gas on hydride of chlorosalicyl (chlorosalicylous acid):

$$3C^7H^5ClO^2 + 2NH^3 = C^{21}H^{15}Cl^3N^2O^3 + 3H^2O.$$

On passing a current of dry ammonia gas over dry chlorosalicylous acid, the gas is absorbed and a yellow resinous mass is formed. To complete the reaction, it is necessary to withdraw the mass from time to time, pulverise it, and again submit it to the action of the gas. The product is then crystallised from absolute alcohol, or better from hot anhydrous ether.

Hydrochlorosalicylamide crystallises in small yellow scales, tasteless, nearly insoluble in water, but soluble in alcohol and ether, especially with aid of heat. Absolute alcohol dissolves it without alteration; but hot aqueous alcohol decomposes it, eliminating ammonia, especially in presence of acid or alkaline liquids.

HYDROSILICITE. A hydrous variety of augite, occurring in amorphous masses or as a crust on the palagonite tufa at Palagonia and Aci Castello in Sicily, associated or mixed with herschelite, phillipsite and calcite. According to v. Waltershausen, it contains 42·02 SiO^2, 4·94 Al^4O^3, 27·19 Ca^2O, 3·41 Mg^2O, 2·51 Na^2O, 2·67 K^2O, 15·06 water and carbonic acid, and 2·19 insoluble matter. (*Rammelsberg's Mineralchemie*, p. 861.)

HYDROSTEATITE. A steatite from Göpfersgrün, in which Klaproth found 59·5 per cent. silica.

HYDROTALCITE. A talc-like mineral, translucent in thin folia, from Snarum in Norway, where it occurs imbedded in serpentine. Hardness = 2·0 (Hochstetter). Specific gravity = 2·091 (Rammelsberg). It dissolves easily and with effervescence in acids, retaining its solubility after ignition. Hermann examined a mineral (which he called *Völknerite*) evidently identical with this, from Scheschemskaja Gora in the Ural, where it occurs in the mica slate, together with chlorospinel, hydrargillite, and other minerals, and is said sometimes to form six-sided prisms cleaving perfectly parallel to the terminal faces. Specific gravity = 2·04.

Analyses. *a.* by Hochstetter (J. pr. Chem. xxvii. 376).—*b*—*e.* by Rammelsberg (*Mineralchemie*, p. 165).—*f.* by Hermann (J. pr. Chem. xlvi. 237).

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Alumina . .	12·00	19·25	17·78	18·00	18·87	16·96
Ferric oxide . .	6·00					
Magnesia . .	36·30	37·27	38·18	37·30	37·04	37·08
Carbonic anhydride	10·54	2·61	6·05	7·32	7·30	3·92
Water . . .	32·66	41·59	37·99	37·38	37·38	42·04
Insoluble residue .	1·20					
	99·60	100·72	100·00	100·00	100·59	100·00

Rammelsberg's and Hermann's analyses, abstracting the carbonic acid, lead to the formula $Al^4O^3.3H^2O + 5—6(Mg^2O.2H^2O)$ or $2Al^2H^3O^3 . 5—6Mg^2H^4O^3$.

HYDROUS ANTHOPHYLLITE. An altered form of asbestiform tremolite (p. 169) found on New York Island and in Scotland.

HYDROZINCITE. See ZINC-BLOOM.

HYDURILIC ACID. $C^8H^6N^4O^6$.—An acid belonging to the uric acid group discovered by Schlieper (Ann. Ch. Pharm. cvi. 11), and further investigated by Baeyer (*ibid.* cxxvii. 11). Schlieper, who assigned to it the formula $C^{12}H^{5}N^{8}O^{11}$, once obtained it accidentally in treating uric acid with dilute nitric acid, and concentrating the mother-liquor remaining after the alloxan (i. 135) had crystallised out; but he did not succeed in preparing it a second time. It was really produced by the decomposition of dialuric acid, which is one of the products of the action of nitric acid upon uric acid (ii. 965), and in Schlieper's experiment was decomposed by the heat of the sand-bath in which the syrupy liquid had been allowed to remain.

Baeyer obtains hydurilic acid by heating dialuric acid with glycerin (which acts merely as a solvent) to about 160°, the dialuric acid then splitting up into hydurilate of ammonium, formic acid, and carbonic anhydride:

$$\underset{\text{Dialuric acid.}}{5C^4H^4N^2O^4} = \underset{\text{Hydurilate of ammonium.}}{2C^8H^5(NH^4)N^4O^6} + CH^2O^2 + 3CO^2.$$

Preparation from Uric acid.—The uric acid is first converted into alloxan by Schlieper's method of oxidation with hydrochloric acid and chlorate of potassium (i. 135); and the alloxan, after being dissolved in lukewarm water, filtered from the unaltered uric acid, and decolorised if necessary with pure animal charcoal, is converted into dialuric acid by reduction with stannous chloride. For this purpose, a quantity of tin equal to the weight of uric acid employed, is dissolved in excess of strong hydrochloric acid; the still hot liquid is added all at once to the alloxan solution; and more hydrochloric acid is added till the volume of the liquid amounts to 4 litres for a pound of uric acid decomposed. The preceding proportions must be carefully observed, for with a smaller proportion of tin, alloxantin is obtained instead of dialuric acid; and unless a large excess of hydrochloric acid is used, dialurate of tin separates in hard crusts, very difficult to decompose. On leaving the strongly acid solution to stand for a day, dialuric acid crystallises out in yellowish stellate groups of short four-sided prisms, which must be quickly washed, and dried in a vacuum. The quantity obtained amounts to about 50 per cent. of the uric acid employed.

To convert the dialuric acid into hydurilic acid, 9 pts. of the perfectly dry substance is mixed in a capacious flask with 5 pts. of concentrated glycerin (as it is obtained by evaporation in a basin till its temperature rises to 160°), and heated in an oil-bath to 140°—150°. A brisk and regular evolution of carbonic anhydride then takes place, and as soon as this ceases and the contents of the flask have become solid, the temperature is raised for a short time to 160°, and the glycerin, after cooling, is removed by washing. A yellowish-white granular powder is then left, consisting of acid hydurilate of ammonium (p. 221). The glycerin takes no part in the reaction, but acts merely as a solvent.

To obtain the free acid, it is best to convert the acid ammonium-salt into a copper-salt and decompose this salt with hydrochloric acid. The crude ammonium-salt is dissolved in boiling water, ammonia is added in slight excess, and solution of cupric sulphate is added to the filtrate. The liquid then assumes a dark-green colour, and, if hot, deposits on cooling red warty crystals of neutral hydurilate of copper. This salt is then decomposed by hot hydrochloric acid, and the hydurilic acid which crystallises out is washed with dilute hydrochloric acid and dried over the water-bath.

Properties.—Hydurilic acid prepared as above forms a bulky white powder having a yellowish tinge; by once re-crystallising it from water, it may be obtained quite pure and colourless. It is very sparingly soluble in cold *water*, somewhat more in hot water, and crystallises therefrom on cooling in small four-sided prisms containing 4 at. water, $C^8H^6N^4O^6.4H^2O$. It is also but very slightly soluble in *alcohol*, which, however, does not precipitate it from the aqueous solution.—*Sulphuric acid* dissolves it without decomposition, and on adding water, part of the hydurilic acid separates out again. In *hydrochloric acid* it is even less soluble than in water, and is gradually precipitated by it from the aqueous solution. From a hot concentrated solution in hydrochloric acid, or from an ammoniacal solution decomposed by hydrochloric acid, it separates as a crystalline powder consisting of rhombic tablets containing 2 at. water of crystallisation: $C^8H^6N^4O^6.2H^2O$. The water, amounting to 6·86 per cent. (2 at. = 6·77) is given off at 140°.

Hydurilic acid bears a tolerably high temperature without decomposition; it likewise offers considerable resistance to the action of *alkalis*, being attacked but slowly and without blackening, by melting potash, with formation of oxalic acid. It is not attacked by reducing agents; but *oxidising agents*, such as *chlorine*, *bromine*, *nitric acid*, *oxide of silver*, *peroxide of lead*, and *sesquichloride of iron*, attack it very quickly, yielding various products. When heated with *ferric chloride*, it yields oxyhydurilic acid, an acid not yet examined, but characterised by the blood-red colour which it produces with ferric salts. With a mixture of *hydrochloric acid and chlorate of potassium*, hydurilic acid yields dichloro-hydurilic acid, $C^8H^4Cl^2N^4O^6$.—Fuming *nitric acid* converts it into alloxan without any other product; but with nitric acid of ordinary strength, it yields alloxan together with violuric acid, violantin and dilituric acid (ii. 965). If the action be carried on to the end, with aid of heat, the only product is dilituric acid*; but if it be interrupted at an earlier stage, a mixture is obtained, varying in composition according to the duration of the action:

$$\underset{\text{Hydurilic acid.}}{C^8H^6N^4O^6} + NHO^3 = \underset{\text{Violuric acid.}}{C^4H^3N^3O^4} + \underset{\text{Alloxan.}}{C^4H^2N^2O^4} + H^2O;$$

$$\underset{\text{Hydurilic acid.}}{C^8H^6N^4O^6} + 2NHO^3 = \underset{\text{Dilituric acid.}}{C^4H^3N^3O^5} + \underset{\text{Alloxan.}}{C^4H^2N^2O^4} + NHO^2 + H^2O.$$

Dilituric acid may indeed be regarded as a product of the oxidation of violuric acid, $C^4H^3N^3O^5 = C^4H^3N^3O^4 + O$; and violantin, $C^8H^6N^6O^9$, is a compound of the two. With *nitrous acid*, the same products are obtained. With nitrite of potassium and excess of nitrous acid, the products are violurate of potassium and alloxan:

$$\underset{\text{Hydurilic acid.}}{C^8H^6N^4O^6} + NKO^2 + 2NHO^2 = \underset{\text{Violurate of potassium.}}{C^4H^2KN^3O^4} + \underset{\text{Alloxan.}}{C^4H^2N^2O^4} + 2H^2O + 2NO.$$

Hydurilic acid is most distinctly characterised by the splendid dark-green colour which the acid and its salts produce in a solution of *ferric chloride*. The colour is destroyed by strong acids and alkalis, also by heat, the hydurilic acid then decomposing and the colour changing to red. Characteristic also are the chalk-white precipitates produced on adding hydrochloric acid to the alkaline solution, and the reactions with hydrochloric acid and chlorate of potassium and with nitric acid, just mentioned.

Hydurilates. Hydurilic acid is dibasic, yielding both acid and neutral salts. It dissolves easily in ammonia, potash, and soda, forming moderately soluble salts; the other hydurilates are sparingly soluble or insoluble. These salts cannot, however, in general be obtained by double decomposition, since the acid has a great tendency to form double salts; they must therefore be prepared with the free acid. The acid decomposes most metallic chlorides, forming acid salts; also acetates, with formation of neutral salts, excepting in the case of the ammonium- and potassium-salts.

Hydurilates of Ammonium.—The *acid salt*, $C^8H^5(NH^4)N^4O^6$, obtained by heating dialuric acid in glycerin (p. 220), is nearly pure, having only a faint yellowish colour. It is moderately soluble in boiling water, and separates, on cooling, in crusts and granules. By solution in hot dilute ammonia, and precipitation with acetic acid, it is obtained quite pure, in small octahedral crystals, which, however, soon lose their form. Strong acids remove only part of the ammonia. The crystals are anhydrous.

The *neutral-salt*, $C^8H^4(NH^4)^2O^6$, is obtained by mixing the acid salt with ammonia, and separates from a hot saturated solution by rapid cooling in needles containing 2 at. water; it is also obtained in the same form by precipitation with sulphide of ammonium, in which it is insoluble. The solution when left to stand, or slowly evaporated, deposits large shining monoclinic prisms, with dihedral summits, containing 4 at. water, and efflorescing, with loss of water and ammonia, when exposed to the air. (For Rammelsberg's determination of the form of these crystals, see Ann. Ch. Pharm. cxxvii. 19.) The salt is moderately soluble in water, very easily in ammonia, and is completely precipitated therefrom by alcohol in amorphous flocks or in needles.

Hydurilate of Barium (neutral), $C^8H^4Ba^2N^4O^6.2H^2O$, is obtained as an amorphous precipitate, which soon becomes crystalline, on adding a hot solution of hydurilic acid to acetate of barium.

Hydurilates of Calcium.—The *acid salt*, $C^8H^5CaN^4O^6.8H^2O$, separates, on adding hydurilic acid to a solution of chloride of calcium, in small shining prisms, insoluble in water. The *neutral salt*, $C^8H^4Ca^2N^4O^6.6H^2O$, is obtained by decomposing acetate of calcium with hydurilic acid, as an amorphous precipitate, which becomes crystalline on standing. It gives off 2 at. water at 130°.

Hydurilates of Copper.—The *acid salt*, $C^8H^5CuN^4O^6.8H^2O$, is obtained by adding cupric acetate to excess of hydurilic acid, or by mixing the acid with cupric sulphate. From concentrated solutions it separates in green needles; from more dilute solutions, in thin prisms of a shining yellow colour. It is decomposed by excess of strong acids. When heated, it gives off the whole of its water, and is converted into a red powder of the anhydrous salt, which is also precipitated immediately from hot solutions.

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* Schlieper's "nitro-hydurilic acid," obtained by the action of hot nitric acid on hydurilic acid, was most probably dilituric acid containing potash, derived from the impure hydurilic acid used. (Baeyer, Ann. Ch. Pharm. cxxvii. 211.)

The *neutral salt*, $C^8H^4Cu^2N^4O^6.8H^2O$, is obtained by adding hydurilic acid to excess of cupric acetate, or by mixing the neutral ammonium- or sodium-salt with cupric sulphate. Cold dilute solutions yield a red precipitate of the hydrated salt, consisting of short needles; warm concentrated solutions, a dark brown-red precipitate of the anhydrous salt. The red salt is converted by heat into the brown salt, giving off its water, but recovers it in contact in water. The salt is decomposed by excess of hydrochloric acid, yielding hydurilic acid and chloride of copper.

Hydurilates of Iron.—The ferric salt is a dark green, easily decomposible precipitate; the *ferrous salt* is a white precipitate which soon turns green.

Hydurilate of Lead is a white precipitate, insoluble in acetic acid, insoluble in water, soluble in nitric acid; obtained by adding hydurilic acid to neutral acetate of lead.

Hydurilate of Potassium has not been obtained in definite form. A solution of hydurilic acid in potash mixed with acetic acid, yields hydurilic acid containing variable quantities of potash; alcohol also throws down from the same solution a substance containing more potash than the neutral salt would contain.

Hydurilate of Silver.—Acetate of silver forms with hydurilic acid small shining prisms, which soon turn grey: with a cold solution of hydurilate of ammonium, it forms a white precipitate; with a warm solution, crystals which soon turn black. On boiling the silver-salt with water, silver is reduced, and the hydurilic acid is oxidised, forming oxyhydurilic acid (p. 221).

Hydurilate of Sodium, $C^8H^4Na^2N^4O^6.H^2O$, is obtained by acidulating a solution of hydurilic acid in strong soda-ley with acetic acid, and adding alcohol. The neutral salt then separates in small, colourless, shining prisms, which are moderately soluble in cold, easily in hot water. The acid-salt does not appear to exist.

Hydurilates of Zinc.—The *acid salt*, $C^8H^5ZnN^4O^6$, crystallises from a solution of zinc-chloride mixed with hydurilic acid, in beautiful feathery groups of needles having a strong lustre. The *neutral salt*, $C^8H^4Zn^2N^4O^6.4H^2O$, separates on mixing hydurilic acid with excess of zinc-solution, as a white amorphous precipitate, which soon becomes crystalline.

Dichlorohydurilic acid. $C^8H^4Cl^2N^4O^6$.—This compound is prepared on adding chlorate of potassium by small portions, and with constant stirring, to a pasty mixture of hydurilic and strong hydrochloric acid. A snow-white powder is thus obtained, which is very slightly soluble in water, either hot or cold, and is most easily purified by dissolving it in strong sulphuric acid, which exerts but little action on it, but thickens when heated with it over the water-bath, and, on gradual addition of water, deposits the chlorinated acid in small rhombic crystals, containing $C^8H^4Cl^2N^4O^6.4H^2O$. It is especially permanent in acid liquids, is not attacked by chlorine, and but slowly by warm nitric acid, with formation of dilituric acid, but is easily decomposed by alkalis.

Dichlorohydurilic acid is a strong dibasic acid, which dissolves in alkalis, especially with aid of heat, and is reprecipitated by hydrochloric acid. The solutions turn red on boiling, yielding a metallic chloride, and an acid not yet examined.

The *neutral potassium-salt*, $C^8H^2K^2Cl^2N^4O^6.4H^2O$, crystallises from a warm solution of potash saturated with the acid in small, beautiful six-sided tables. It dissolves sparingly in cold, more readily in hot water. It retains its water of crystallisation at 120°; at a stronger heat it turns red and decomposes.

HYGRINE. (Wöhler and Lossen, Ann. Ch. Pharm. cxxi. 374.—Lossen, *Dissertation.*)—An organic base occurring, together with cocaïne, in coca-leaves (i. 1059). To extract the two bases, the leaves are exhausted with rain-water at a temperature of 60° to 80°; the united extracts are precipitated with neutral acetate of lead and filtered; the filtrate is precipitated with a saturated aqueous solution of sulphate of sodium, again filtered and concentrated; and the concentrated liquid, after being rendered slightly alkaline by carbonate of sodium, is agitated four or six times with ether to extract the cocaïne. The remaining liquid mixed with an additional quantity of carbonate of sodium, and again shaken with ether, yields hygrine and a neutral oil having the odour of tobacco. These substances remain when the ether is distilled off; and on further heating the residue, till it boils, the temperature quickly rises to above 280°, and a brown alkaline oil distils over, while a black resin is left behind. When the distillate is maintained at 140°, for some hours, in a stream of hydrogen, the greater part passes over of a yellow colour (*a*), while the remainder volatilises only at 140° to 230°, and condenses to a thick brown oil (*b*). Hygrine is contained in both portions; that in *b*, however, is contaminated with a neutral oil;

that in *a* with an easily volatilised substance. To remove a little ammonia present, *a* is converted into oxalate, the salt is dissolved in absolute alcohol, the solution evaporated, and the residue mixed with caustic potash, which separates the hygrine in the form of oil. The alkaline solution is heated to boiling in a stream of hydrogen, when the hygrine, dissolved in the water, passes over (by adding water to the residue and again distilling to dryness, a further quantity may be obtained), and is extracted from the distillate by ether; on again distilling the ethereal solution, the hygrine remains behind. The neutral oil in *b* is removed by dissolving *b* in water containing hydrochloric acid, shaking the solution with ether, and separating the ethereal layer; after which, the acid solution is supersaturated with caustic soda, and the hygrine taken up by ether, as in the treatment of *a*. (Lossen.)

Hygrine is a thick, pale-yellow oil, having a strong alkaline reaction, a burning taste, and an odour of trimethylamine. It produces white clouds with the volatile acids; distils very slowly with vapour of water. It does not appear to be poisonous.

Hygrine does not dissolve in *water* in all proportions. The aqueous solution forms a white precipitate with *dichloride of tin*, yellowish with *sulphate of iron*, light blue with *sulphate of copper;* on boiling the solution, the copper precipitate becomes granular, but not brown. Hygrine forms white precipitates with *chloride of mercury* and *nitrate of silver;* the silver precipitate quickly turns brown.

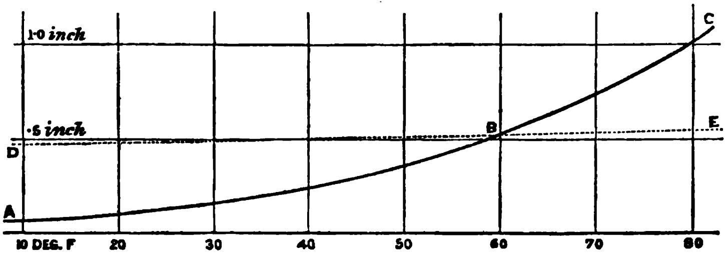
Hygrine combines with *hydrochloric acid*, forming deliquescent crystals. The aqueous hydrochlorate forms a brown flocculent precipitate with *di-iodide of potassium*, red-white with *dichloride of tin*, white with *corrosive sublimate*, partly flocculent and partly in oily drops. With *dichloride of platinum* it forms dirty white-yellow (or red) flakes, which are decomposed by heating the liquid, and do not appear in very dilute solutions. *Picric acid* throws down from hydrochlorate of hygrine a yellow powder; *gallotannic acid*, a white poecipitate.

Hygrine dissolves in *alcohol* and in *ether*.

HYGROMETER. HYGROMETRY. A Hygrometer (*ὑγρός*, moist; *μέτρον*, measure) is any instrument which measures the amount or degree of moisture in the atmosphere. There are, however, several kinds of hygrometers which measure, or are said to measure moisture, by entirely different modes, and the problem itself—to estimate the degree of moistness of the air—is found on examination to be quite ambiguous. It is therefore necessary to attend to the principles of the subject.

Principles of Hygrometry.—Water, both liquid and solid, always tends to assume the gaseous form, and in so doing exerts an elastic force increasing as the temperature rises. In *fig.* 565 the curve ABC is drawn so as to represent the law of the elastic force of aqueous vapour: if the divisions along the horizontal axis represent the temperature of the water in degrees Fahr., the perpendicular lines drawn from them to the curve, being measured, will give the corresponding force of its vapour estimated in the height of the column of mercury which it would be able to sustain.

Fig. 565.



The elastic force obviously increases in a higher ratio than the temperature, and, in order that such increasing force may be exerted when water is confined in a given space, it is necessary that a larger and larger quantity of water should become vapour. It is true that if the weight of vapour be not increased, its elastic force will rise with its temperature, but in a much less ratio. For aqueous vapour, like any other gas, tends to expand by $\frac{1}{491}$th part of its volume at 32° F. for every degree of increased temperature. Thus, if the vapour which rises from water at the temperature of 60° F. and has the elastic force of ·518 inch be confined in the same space, but apart from water, and heated, its elastic force will rise in a manner represented by the straight line BE (*fig.* 565); but if more water be present to supply additional vapour, the elastic force of the whole vapour would rise, as shown by the curve BC.

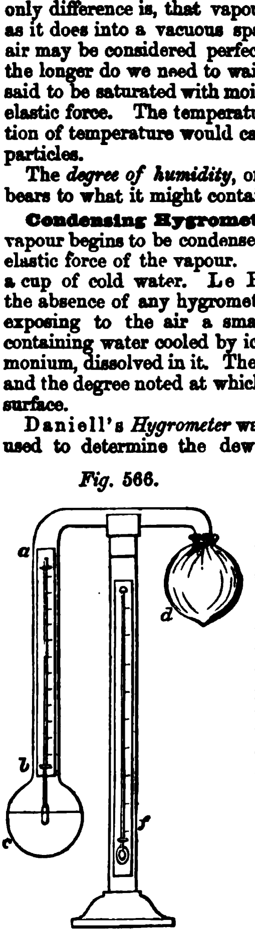
On the other hand, if the vapour at 60° F. be cooled, it will, as a gas, tend to exert an elastic force falling as the straight line BD. But the elastic force which liquid water exerts falls more rapidly, as shown by the curve BA; hence part of the vapour must be condensed to the liquid condition until the elastic force of the remainder is not greater than that which rises from water at that temperature. The following definitions will now be understood. Aqueous vapour is said to be *saturated*, and of *maximum elastic force*, when any reduction of temperature, or any increase of pressure, would cause some of the vapour to be condensed. The temperature of saturated vapour is said to be at the dew-point. Thus aqueous vapour of 60° F. and of an elastic force of ·518 inch is saturated, and 60° is its dew-point. Any portion of aqueous vapour has a dew-point; for the temperature may always be reduced so low that a portion will be condensed by any further reduction.

What is true of aqueous vapour alone is also true of aqueous vapour mixed with air: for it is a law that mixed gases do not exert their pressure upon each other. The only difference is, that vapour does not spread so rapidly into a space occupied by air as it does into a vacuous space. In an *indefinitely small space*, then, the vapour and air may be considered perfectly independent of each other. The larger the volume, the longer do we need to wait until diffusion has produced perfect mixture.* Air is said to be saturated with moisture when the aqueous vapour it contains is of maximum elastic force. The temperature of the air is then called its dew-point—for any reduction of temperature would cause the condensation of some vapour in the form of *dewy* particles.

The *degree of humidity*, or *of saturation*, is the ratio which the vapour in the air bears to what it might contain. (See HEAT, pp. 81, 83.)

Condensing Hygrometers are those which, by cooling the air until the contained vapour begins to be condensed, indicate the dew-point, and thus enable us to learn the elastic force of the vapour. Dalton first proposed this method of Hygrometry, using a cup of cold water. Le Roi proposed the use of ice for this purpose; and in the absence of any hygrometer, the dew-point may be ascertained very accurately, by exposing to the air a small bright metal cup, for instance a platinum crucible, containing water cooled by ice or by some salt, such as sal-ammoniac or nitrate of ammonium, dissolved in it. The water is to be stirred with the bulb of a small thermometer, and the degree noted at which dew begins to form or to evaporate on the bright metallic surface.

Fig. 566.



Daniell's *Hygrometer* was the first accurate instrument invented, and may still be used to determine the dew-point with considerable ease and exactness (*Daniell's Meteorological Essays*, p. 127). It consists (*fig.* 566) of a small glass siphon, at each end of which is a thin glass bulb about 1¼ inch in diameter. The longer leg *ab* is about 4 inches long and contains a small but very delicate thermometer, the bulb of which is within the terminal glass ball. The siphon contains so much common ether as when poured into the lower bulb *c* will rather more than half cover the enclosed thermometer-bulb. Before the tube is sealed up, the ether is boiled, so as to drive out the whole of the air. The essential part of the instrument is completed by covering the upper bulb *d* with muslin and gilding a part of the lower bulb. It is now usual, however, to make this lower bulb of black glass. The siphon-tube is placed for use upon the little stand which contains the second thermometer *f*, in order that the temperature of the air may be observed at the same time as its dew-point.

To make an observation, all the ether within the instrument is first poured into the lower bulb. Then taking a bottle of common ether, a few drops are poured upon the muslin of the upper bulb. Its evaporation cools the bulb and condenses the ether vapour within. Fresh vapour flows along the bent tube from the lower bulb, and, in the manner of Wollaston's *cryophorus*, the temperature of this lower bulb is gradually reduced, until the dew-point of the surrounding air is reached, and dew may be observed forming upon the gilded or blackened surface of the bulb. The dew-point, as shown by the included thermometer, is then to be read, but accuracy is only to be attained by observing several successive depositions and evaporations of dew in a manner fully described under the head of Regnault's Hygrometer.

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* A neglect of this fact has led many eminent meteorologists to consider the atmosphere as composed of two independent atmospheres, namely of aqueous vapour and of the other gases. Nothing can be more erroneous.

The hygrometer of Daniell, however elegant and pleasing in theory, has many sources of inconvenience and inaccuracy. The expenditure of ether is considerable and costly, and in a hot and dry climate it is very difficult to obtain any deposition of dew, during the long-continued manipulation and close observation of the instrument which is always necessary. The warmth and moisture of the hand and body are sure to affect the indications of both thermometers. The cold ether vapour flowing from the upper bulb may also cause inaccuracy. The last and most important objection is that cold is produced only at the surface of the ether in the lower bulb, and there is no agitation of the liquid to ensure uniformity of temperature. Hence the internal thermometer may often indicate a temperature some degrees different from that at which dew is being deposited. This objection is partially remedied by making the lower bulb oblique, so that one part of it shall be nearly in contact with the thermometer-bulb within. Daniell, well aware of this objection, remarks that dew will first be deposited in a circle round the bulb near to the surface of the ether, and directs that the thermometer-bulb shall be placed so as to be cut by the surface of the ether.

Subsequent to Daniell's invention, several dew-point instruments were devised, in which the evaporation of ether was made to cool the bulb of a thermometer and cause a deposit of dew, either upon the bulb or a metallic capsule in a more simple manner. Such is that of Jones (Phil. Trans. [1826] cxvi. pt. ii. 53). Of a similar nature are the *hygromètre à capsule* and the *hygromètre à virole d'or* of Pouillet (Élém. de. Phys. [7th ed. 1856] ii. 739). That of M. Belli (Ann. Ch. Phys. [3] xv. 506) is different and very ingenious, giving a continual indication of the dew-point.

Connell's *Hygrometer*, very lately proposed, and to some extent, we believe, brought into use, consists of a thermometer with its bulb immersed in ether, contained within a small metal globe. A common exhausting syringe is used to cause the evaporation of the ether, and the dew-point is then ascertained, exactly as in Daniell's or Regnault's hygrometer. This method presents some slight advantages over Daniell's, but retains all its worst causes of error and inconvenience. It is also an expensive instrument, and cannot compare with Regnault's Condenser Hygrometer either in theory or in practice. It is described in the Transactions of the Royal Society of Edinburgh xxi., and Phil. Mag. [4] viii. 81.

Dr. George Cumming's *Hygrometer* (Quar. Jour. of Sci. &c. 1828, Jan. to June, p. 403) seems first to have introduced a method now finally adopted as the best. It consisted (*fig.* 567) of a thin glass or metallic tube containing a delicate thermometer enveloped in sponge or other porous substance, upon which a little ether was to be poured. Almost any degree of artificial cold could then be produced by a stream of air from a pair of bellows, or other pneumatic contrivance. The only important objection to this instrument is the presence of a spongy or porous substance, which would prevent perfect uniformity of temperature within the tube.

Fig. 567.

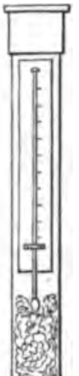
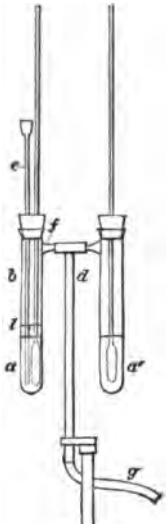


Fig. 568.



Döbereiner further proposed a hygrometer in which a current of air from a forcing pump is made to traverse the ether, disposed as in Daniell's instrument, and thus produce cold by evaporation. (Pogg. Ann. lxv. 339.)

Regnault's *Condenser Hygrometer* (Ann. Ch. Phys. [3] xv. 129) may be described as a perfect instrument of its kind. In its complete form (*fig.* 568) it consists of a very thin and brightly polished silver thimble *a*, 45 mm. high and 20 mm. in diameter, fitted to the glass tube *b*, which again is fixed by the small lateral tube *t*, and the metallic tube *d*, to the stand. The upper end of the glass tube *b* is closed by a cork, bearing a thin glass tube *e*, descending nearly to the bottom of the silver thimble, and a very delicate and accurate thermometer, the pear-shaped bulb of which is in the centre of the thimble. A second exactly similar thermometer, similarly placed within a glass tube and silver thimble, is mounted on the other side of the stand, but the cork is not penetrated by any glass tube.

To make an observation, so much good ether is poured into the tube *b* as will rather more than fill the thimble to the level *l*, and the cork being fitted in air tight, the instrument is put in connection, by means of the caoutchouc tube *g*, with a common aspirator, by which an exactly regulated flow of air through the instrument may be obtained. The aspirator, which may have a capacity of 3 or 4 litres (3 or 4 quarts) is placed close to the observer, and the hygrometer may be at some distance, for instance outside a window, being observed, if necessary, with a telescope.

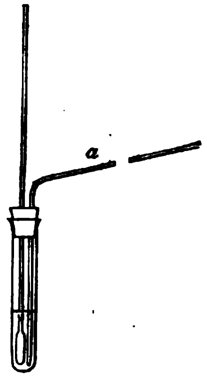
Now when water is allowed to flow from the aspirator, air is drawn through the tube, and bubbling up through the ether, causes a more or less rapid evaporation. The temperature of the ether is thus slowly reduced, and from its constant agitation by the stream of air, the silver thimble and the thermometer-bulb are maintained at an exactly similar temperature. After a minute or two at the most, dew will begin to form on the thimble and will be very visible on its brightly polished surface. The thermometer is instantly to be read, and the stream from the aspirator to be stopped. Suppose that the reading observed is 48·1° F., the deposit of dew may increase for a few moments, but will soon begin to evaporate again, the thermometer rising. At the moment that the dew entirely disappears, read the thermometer again; let it be 49·3. Considering that dew requires a short time to form or evaporate in a visible degree, it is obvious that the dew-point lies between 48·1 and 49·3. Let an exceedingly slow current of air be now drawn through the ether, so that the thermometer is very gradually reduced to 49·2, 49·1, 49·0, and so on. The point at which dew first appears may now be observed with much greater accuracy; let it be 48·8. Still it is probable that 48·8 is somewhat below the exact dew-point. If, when the current is stopped, the small deposit of dew vanishes at 49·0, we may consider the mean, or 48·9, to be the true dew-point; but if necessary we may, by still slower procedure, approximate even more closely. "All these operations," observes M. Regnault, "take more time to describe than to execute; with a little practice, three or four minutes are sufficient for determining the dew-point almost within $\frac{1}{20}$ of a degree Centigrade."

At the same time, the second thermometer is to be read, to give the common temperature of the air. From its parallel circumstances and position, its indications would be exactly similar to those of the other; hence the difference of the two gives the depression of the dew-point free from almost all kinds of error. It is obvious that all the objectionable points in Daniell's hygrometer are avoided in this admirable instrument. The only remaining objection is the inconvenience of keeping or carrying about a large aspirator, and frequently filling it with water. In the Kew Observatory, the aspirator is in the form of a circular bellows, to the lower movable board of which a weight is attached. Mr. Welsh also proposed to expand the upper end of the tube *e* into a small funnel by which fresh ether may readily be introduced.

Lieut. Noble has obtained dew with this hygrometer, at all temperatures down to −35°, the limit of graduation of his thermometer, the only requisites when the dew-point is very low being patience and pure ether. (Phil. Mag. [4] xi. 305.)

Several London instrument-makers have rendered this instrument less expensive by omitting the second thermometer and its appendages. They have likewise substituted a closed tube of black glass for the polished silver thimble. This is, on the whole, an improvement, for the dew is even more visible on the black surface, and the difficulty of maintaining the silver bright is avoided; but on the other hand the uniformity of temperature is not so rigorously ensured. As regards the temperature of the air, we think it is best learnt by an ordinary thermometer freely exposed, and that Regnault's parallel arrangement of the second thermometer, although beautiful in theory, is actually erroneous and undesirable in the ordinary use of the instrument.

Fig. 569.



Except, however, for refined researches or long continued series of observation, a much simpler apparatus will serve. The practical chemist has only to take a common test-tube, containing about 1½ inch depth of ether, insert somewhat loosely a delicate tube-thermometer and glass tube, as shown in *fig.* 569, and gently blow with the mouth through the bent tube *a*, and the whole process of observation can be conducted almost as well as in Regnault's complete instrument. It is necessary to have the tube *a* of considerable length, that the moistness and warmth of the body and the breath may not affect the air surrounding the tube. The writer had used such an apparatus daily for many months before noticing that Regnault mentions its successful use.

Hygrometry by Evaporation.—Dr. Hutton of Edinburgh first suggested that the degree of cold produced by the evaporation of water in the air, would depend upon and therefore indicate the moistness of the air. Leslie again very distinctly stated this principle (Leslie, *On the Relations of Air to Heat and Moisture*, 1813, p. 39), and reduced it to practice by covering one of the bulbs of his differential air-thermometer with wet muslin. The motion of the column of water towards the moist bulb, of course, shows the depression of the temperature of evaporation. This hygrometer might yet, we think, be often used in certain researches, and might be added to the common weather-glass.

The Dry- and Wet-Bulb Hygrometer, called on the Continent the *Psychrometer* (ψυχρός, cold; μέτρον, measure), is formed of two similar delicate thermometers placed in a gentle current of air, the bulb of one thermometer being covered with muslin and kept moist by a cotton thread leading from a small reservoir of rain or distilled water. The dry-bulb thermometer indicates the true temperature of the air; the other will be found to remain stationary at a temperature said to be that of evaporation, which is usually several degrees below that of the air. In saturated or moist air, the thermometers read alike; the difference increases in some proportion to the *dryness* of the air, and may be used as a sufficient measure of the dryness in many practical matters, such as the ventilation of dwelling-houses, halls, plant-houses and so on.

From observations of the dry- and wet-bulb thermometers, it is further possible, by means of tables previously determined by experiment, or by calculation from *à priori* principles, to determine the existing tension of aqueous vapour, and other hygrometric data. The most trustworthy table for such reductions is the following, which has been obtained by Mr. Glaisher from the combination of all the simultaneous observations of the dry- and wet-bulb thermometers with Daniell's hygrometer, taken at the Royal Observatory, Greenwich, from the year 1841 to 1854, with some observations taken at high temperatures in India, and others at Toronto.

TABLE I. *To obtain the dew-point, multiply the difference of reading of the thermometers by the factor opposite the dry-bulb reading, and subtract the product from the dry-bulb reading.*

Dry-bulb thermometer F.	Factor.	Dry-bulb thermometer F.	Factor.	Dry-bulb thermometer F.	Factor.	Dry-bulb thermometer F.	Factor.
10°	8·78	33°	3·01	56°	1·94	78°	1·69
11	8·78	34	2·77	57	1·92	79	1·69
12	8·78	35	2·60	58	1·90	80	1·68
13	8·77	36	2·50	59	1·89	81	1·68
14	8·76	37	2·42	60	1·88	82	1·67
15	8·75	38	2·36	61	1·87	83	1·67
16	8·70	39	2·32	62	1·86	84	1·66
17	8·62	40	2·29	63	1·85	85	1·65
18	8·50	41	2·26	64	1·83	86	1·65
19	8·34	42	2·23	65	1·82	87	1·64
20	8·14	43	2·20	66	1·81	88	1·64
21	7·88	44	2·18	67	1·80	89	1·63
22	7·60	45	2·16	68	1·79	90	1·63
23	7·28	46	2·14	69	1·78	91	1·62
24	6·92	47	2·12	70	1·77	92	1·62
25	6·53	48	2·10	71	1·76	93	1·61
26	6·08	49	2·08	72	1·75	94	1·60
27	5·61	50	2·06	73	1·74	95	1·60
28	5·12	51	2·04	74	1·73	96	1·59
29	4·63	52	2·02	75	1·72	97	1·59
30	4·15	53	2·00	76	1·71	98	1·58
31	3·70	54	1·98	77	1·70	99	1·58
32	3·32	55	1·96				

As an example, let the dry-bulb thermometer stand at 64·3° F., and the wet-bulb at 60·8°:

$$64·3 - 60·8 = 3·5 = \text{difference of readings.}$$

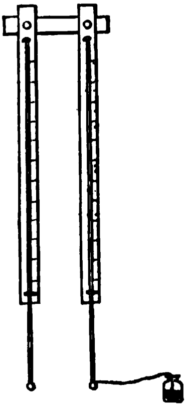
The factor to be used is 1·83 opposite 64°, the nearest degree to 64·3:

$$64·3 - 3·5 \times 1·83 = 57·9° = \text{dew-point.}$$

In the Phil. Mag. [4] xi. 304, is a table for reduction of dry and wet-bulb readings from 51° F. down to − 16°, giving also the probable error and measure of precision of the results determined by Lieut. Noble from observations at Toronto.

The dry- and wet-bulb thermometer having long become the ordinary working hygrometer of the meteorological observer, Mr. Glaisher has paid much attention to the perfecting of the instrument in every detail. He has finally adopted a pair of very delicate thermometers (see *fig.* 570) about one foot long, and with small spherical bulbs of thin glass of about ¼ inch diameter. They are mounted upon metal scales graduated from about −10° to +130° F. and fixed parallel to each other from 2 to 4 inches apart upon a metal cross piece. Care is taken that each pair of thermometers is as exactly similar as possible. The bulb of the wet thermometer is covered with thin muslin, round the neck of which is twisted a conducting thread of lamp wick, common darning cotton, or floss silk; this passes into an adjacent vessel of water placed about three inches distant from the wet bulb, a little beneath it, and on the opposite side to the dry-bulb thermometer. It is a very objectionable practice to place a long glass cistern between the two thermometers; for the water will seldom be of exactly the same temperature as the surrounding air, and will tend slightly to vitiate the readings of both thermometers. The writer prefers for a cistern a short narrow-necked glass bottle, from which but little evaporation will take place. The water must be either rain or distilled water. Care must be taken never to record any readings when the bulb is not thoroughly moist all over. As dust and saline particles gradually settle on the wet muslin, it is well to re-cover the bulb and supply a fresh wick about every month. Before use, too, each wick should be washed in a solution of carbonate of soda, and pressed whilst under water throughout its length. The supply of water to the bulb can be easily regulated by raising or lowering the cistern.

Fig. 570.



In taking an observation, the dry-bulb thermometer is first to be read, because it is most liable to change; the wet-bulb is then to be read, the two readings to be recorded, and a comparison with the thermometers made, to secure the correct number of whole degrees. The observer must follow the directions under the article THERMOMETER, as regards placing the instrument, correcting the thermometer-readings, &c.

The dry- and wet-bulb hygrometer continues to act even when the water is frozen, since evaporation still takes place; but especial care must be taken that the bulb really is covered with ice, and if not, water must be poured upon it, and the observation delayed till the water be frozen, and the thermometer sink to a constant reading. In frosty weather it is best to wet the bulb after every periodic observation, or at least ten minutes before the next.

Theory of the Psychrometer.—Although we may ascertain the dew-point from readings of the dry- and wet-bulb thermometers on purely experimental grounds, as in using Glaisher's factors, the subject also admits of mathematical investigation. Mr. Ivory first solved the problem (Phil. Mag. [3] lx. 80) with substantial correctness. August of Berlin, and Bohnenberger, showed the coincidence of the theory with experiment, and determined the constants with accuracy (August, *Ueber die Fortschritte der Hygrometrie in der Neuesten Zeit, Berlin*, 1830.—Bohnenberger, *Tubingen Nat. Hist. Soc. Memoirs*, vol. ii.). But the subject is best known in England from Dr. Apjohn's excellent results (Phil. Mag. [3] vi. 182; vii. 266, 470; xiii. 261).

We now give the investigation as it is stated by Regnault after the method of M. August.

The evaporation of a liquid involves the conversion of sensible into latent heat, and the supply of heat must be drawn from the liquid evaporated, from the remaining liquid, or from surrounding objects. When air is in contact with the moistened bulb of a thermometer, the evaporation of the water will reduce the temperature of the bulb, but the fall of temperature will be checked by heat communicated from the remainder of the air. At some point, the amounts of heat subtracted and communicated will be equal, and an invariable temperature of evaporation will be the result.

Let us suppose, with M. August, that the portions of air successively in contact with the moist thermometer-bulb become thereby perfectly saturated with moisture, and are reduced to the temperature of the bulb.

Let w = weight of stratum of dry air surrounding the bulb at 0° C., and under the pressure of 0·760.
h = height of barometer.
t = temperature of surrounding air given by the dry-bulb thermometer.
t' = temperature of evaporation, or the reading of the wet-bulb thermometer.
f and f' = the elastic forces of saturated aqueous vapour for the temperatures t and t'.
x = the actual elastic force of vapour in the air at the time.

In the stratum of air surrounding the bulb, the aqueous vapour exerts the elastic force f', and the air consequently exerts the elastic force $h-f'$. The weight of dry air is then

$$w \cdot \frac{1}{1+\alpha t'} \cdot \frac{h-f'}{30},$$

α being the coefficient of expansion of a gas for every degree of temperature. The weight of vapour already in this air is

$$w\,\delta \cdot \frac{1}{1+\alpha t'} \cdot \frac{x}{30};$$

in which δ represents the specific gravity of aqueous vapour in relation to air. The weight of vapour added by contact with wet bulb similarly is

$$w\,\delta \cdot \frac{1}{1+\alpha t'} \cdot \frac{f'-x}{30}.$$

Now, if γ be the specific heat of air, the quantity of heat disengaged by the dry air in cooling from t to t' is

$$w \frac{1}{1+\alpha t'} \cdot \frac{h-f'}{30} \cdot (t-t') \,.\, \gamma.$$

Similarly k being the specific heat of aqueous vapour, the quantity of heat disengaged by the vapour previously in the air is

$$w\,\delta \frac{1}{1+\alpha t'} \cdot \frac{x}{30}(t-t') \,.\, k.$$

Lastly, let λ be the latent heat absorbed by water, when becoming gaseous between the temperatures t and t'.

The quantity of heat absorbed will be

$$w\,\delta \frac{1}{1+\alpha t'} \cdot \frac{f'-x}{30} \cdot \lambda.$$

Now when the temperature of evaporation is constant, this heat absorbed in evaporation must be equal to that given out by the air and the other portion of vapour; or we have, by equating them and striking out the factor $w \cdot \frac{1}{1+\alpha t'} \cdot \frac{1}{30}$,

$$\gamma\,(h-f')(t-t') + \delta\,k\,x\,(t-t') = \delta\,\lambda\,(f'-x);$$

whence

$$x = \frac{1 + \frac{\gamma}{\delta\lambda}(t-t')}{1 + \frac{k}{\lambda}\,(t-t')} f' - \frac{\frac{\gamma}{\delta\lambda}(t-t')}{1+\frac{k}{\lambda}(t-t')} \cdot h.$$

Inserting values of the known quantities, namely, for γ, 0·2669, for k, 0·2669 (the specific heat of aqueous vapour being assumed equal to that of air), for δ, the specific gravity of aqueous vapour, 0·6235, and for λ, the latent heat of aqueous vapour, $640-t'$, according to the law of Watt, and neglecting some of the smaller terms, August obtains the formula $x = f' - \frac{0·568\,(t-t')}{640-t'} \cdot h$, the temperatures being expressed in centigrade degrees.

Regnault, using more accurate data, namely, for δ, 0·622, and for λ, $610-t'$ ($\gamma = k = 0·2669$ as before), modifies this to

$$x = f' - \frac{0·429\,(t-t')}{610-t'} \cdot h.$$

Experimentally, Regnault has found that the formula $x = f' - \frac{0·480\,(t-t')}{610-t'} \cdot h$ gives an almost perfect coincidence between the calculated and true results, when the air is not more than $\frac{4}{10}$ saturated. Otherwise the first coefficient 0·429 is to be preferred.

The formula which has been most used in the reduction of dry- and wet-bulb observations is that obtained by Dr. Apjohn. In the Greenwich observations it is given as follows:

$$F = f - \frac{d}{88} \cdot \frac{h}{30} \qquad F = f - \frac{d}{96} \cdot \frac{h}{30}$$

The first formula is to be used when the reading of the wet-bulb is above 32° F., and the second when below. In the above, d is the difference of the dry- and wet-bulb readings, h the height of the barometer, f the elastic force of vapour for the temperature of the *wet-bulb*, to be taken from Table II., and F the elastic force of vapour at the dew-point, from which the dew-point may be found, if necessary, by the table.

From a statement in *Daniell's Meteorology* [Essays, 1856] ii. 100, it would seem that the errors of results obtained by Apjohn's formula, lie within closer limits than those obtained by Glaisher's factors.

Taking the expression in the form

$$F = f - m.d.\frac{h-f}{30},$$

the term with $\frac{f}{30}$ being inconsiderable except at great heights, the following values of the coefficient m have been given (for degrees Fahr.):

Ivory	·0139
Apjohn—*à priori* calculation	·01149
„ experiments on dew-point	·01151
„ „ refrigeration	·0115
„ other experiments	·0114
Bohnenberger—first 56 observations	·0114
„ second 45 „	·011398
Kaemtz above 32° F.	·0118
„ below 32 F.	·0112
Kupffer above 32 F.	·01135

The supposed great accuracy of many of these determinations has been somewhat shaken by the later experiments of Regnault (Ann. Ch. Phys. [3] xv.), for he finds that the temperature of evaporation is not invariable, but sinks lower, the greater the rapidity with which the air surrounding the wet bulb is moving. He is thus led to doubt the soundness of August's assumption, that the stratum of air surrounding the wet bulb is always saturated and of the same temperature as the bulb, and he considers that the radiant heat falling on the bulb is an element not to be neglected. The ordinary formulæ, however, may be considered sufficiently accurate as long as the velocity of the air does not exceed 5 or 6 metres (16 to 20 feet) per second.

We quite agree, however, with Dr. Drew ("Practical Meteorology," p. 169), that the problem of the dry- and wet-bulb thermometers is still quite open to fresh investigation.

Hygrometric Calculations.—Having found the dew-point of the air, it is usually required to deduce other data concerning the moistness of the air. The necessary calculations are a little intricate, but have been brought to a very satisfactory state of accuracy by Mr. Glaisher, whose excellent hygrometrical tables for the dry- and wet-bulb thermometers, give all the necessary deductions from the readings of the thermometers, almost without calculation. These tables are quite indispensable to any person who has frequently to make hygrometrical calculations, but the ingenious hygrometric sliding rule of Mr. Welsh (Brit. Assoc. 1851; Trans. Sec. p. 42), as manufactured by Adie, will also give most of the required results mechanically. We can here only enter the subject briefly.

The elastic force of aqueous vapour in the air is the same as the maximum elastic force at the dew-point, and we, therefore, ascertain it by referring to the temperature of the dew-point in a table of the maximum elastic force of vapour. The following table (II.), having been calculated from the experimental results of Regnault, is the most reliable of the kind.

If there be a fractional part of a degree over, multiply it into the next following *difference* in the third column (dividing by 10 if a decimal), and add the result to the number opposite the whole degree.

This table differs somewhat from that adopted by the Royal Society in their "Report on Physics" (p. 89), and from several others calculated from older and less trustworthy experiments than those of Regnault.

To find the weight of a cubic foot of aqueous vapour of maximum tension at any temperature t, let E_t be the elastic force at that temperature. Then since 258·448 grains is the weight of a cubic foot of vapour at 212°, of an elastic force of 30 inches, 258·448 grains × $\frac{E}{30}$ would be the weight of a cubic foot of the vapour saturated at temperature t, after it has been heated up to 212° and kept under the same pressure E_t as before. Since a gas expands 0·3665 of its own volume from 32° to 212°, or 0·0020361 for each degree Fahr.,

$$258{\cdot}448 \text{ grains} \times \frac{E_t}{30} \times \frac{1{\cdot}3665}{1 + {\cdot}0020361 \times (t - 32^\circ)}$$

will be the weight of a cubic foot of vapour saturated at the temperature t. From this formula, the numbers in Table III. (p. 232), column 2, were obtained.

When the air is saturated with vapour and the temperature of the air of evaporation and of the dew-point coincide, the required weight of vapour in a cubic foot of air may

Table II. *Showing the Maximum Elastic Force of Aqueous Vapour in inches of Mercury for every degree Fahr. from* 0° *to* 100°.

Temperature. °F.	Force of vapour. Inch mercury.	Difference.	Temperature. °F.	Force of vapour. Inch mercury.	Difference.	Temperature. °F.	Force of vapour. Inch mercury.	Difference.
0	·044	2	34	·196	8	68	·684	24
1	·046	2	35	·204	8	69	·708	25
2	·048	2	36	·212	8	70	·733	26
3	·050	2	37	·220	9	71	·759	26
4	·052	2	38	·229	9	72	·785	27
5	·054	3	39	·238	9	73	·812	28
6	·057	3	40	·247	10	74	·840	28
7	·060	2	41	·257	10	75	·868	29
8	·062	3	42	·267	10	76	·897	30
9	·065	3	43	·277	11	77	·927	31
10	·068	3	44	·288	11	78	·958	32
11	·071	3	45	·299	12	79	·990	33
12	·074	4	46	·311	12	80	1·023	34
13	·078	4	47	·323	12	81	1·057	35
14	·082	4	48	·335	13	82	1·092	36
15	·086	4	49	·348	13	83	1·128	37
16	·090	4	50	·361	13	84	1·165	38
17	·094	4	51	·374	14	85	1·203	39
18	·098	5	52	·388	15	86	1·242	40
19	·103	5	53	·403	15	87	1·282	41
20	·108	5	54	·418	15	88	1·323	43
21	·113	5	55	·433	16	89	1·366	44
22	·118	5	56	·449	16	90	1·410	45
23	·123	6	57	·465	17	91	1·455	46
24	·129	6	58	·482	18	92	1·501	47
25	·135	6	59	·500	18	93	1·548	48
26	·141	6	60	·518	19	94	1·596	50
27	·147	6	61	·537	19	95	1·646	51
28	·153	7	62	·556	20	96	1·697	54
29	·160	7	63	·576	20	97	1·751	55
30	·167	7	64	·596	21	98	1·806	56
31	·174	7	65	·617	22	99	1·862	56
32	·181	7	66	·639	22	100	1·918	
33	·188	8	67	·661	23			

be taken at once from the formula or table. In all other cases, however, since vapour above its dew-point expands like any other gas, we must have

$$\left.\begin{array}{l}\text{Actual weight of a}\\ \text{cubic foot of vapour}\end{array}\right\} = \left.\begin{array}{l}\text{Weight of a cubic foot}\\ \text{of vapour at dew-point}\end{array}\right\} \times \frac{\text{Volume at dew-point}}{\text{volume at temperature of air.}}$$

The weight of a cubic foot of dry air is easily calculated from the following data of Regnault. Dry air expands by $\frac{1}{491 \cdot 13}$ or ·0020361 parts of its volume at 32° F. for every increase of 1° of heat, and a cubic foot of dry air at 32° under a pressure of 30 inches of mercury weighs 566·85 grains. Thus are calculated, for a pressure of 30 inches of mercury, the numbers in column 3 of Table III.

If a cubic foot of dry air and a cubic foot of aqueous vapour of the same temperature be mixed together and compressed into a cubic foot of space, the elastic force of the mixture will be the sum of the elastic forces of the air and vapour. In order that the mixed or moist air may have the same elastic force as the dry air previously, it must be allowed to expand, in the proportion of the elastic force of the dry air to the sum of the elastic forces of the air and vapour.

Thus, if E_t = elastic force of vapour at temperature t,

and p = elastic force of moist air—say the atmospheric pressure as shown by the barometer

we have $p - E_t$ = elastic force of dry air,

and

$$\frac{\text{volume of moist air}}{\text{volume of dry air}} = \frac{p}{p - E_t}.$$

TABLE III.

1	2	3	4	1	2	3	4
Temperature °F.	Weight of a cubic foot of saturated vapour. Grains.	Weight of a cubic foot of dry air. Grains.	Weight of a cubic foot of air saturated with vapour. Grains.	Temperature. °F.	Weight of a cubic foot of saturated vapour. Grains.	Weight of a cubic foot of dry air. Grains.	Weight of a cubic foot of air saturated with vapour. Grains.
0	0·55	606·37	606·03	56	5·04	540·45	537·45
5	0·68	599·83	599·40	57	5·21	539·40	536·30
10	0·84	593·44	592·94	58	5·39	538·36	535·15
15	1·04	587·18	586·55	59	5·58	537·32	534·00
20	1·30	581·05	580·26	60	5·77	536·28	532·84
25	1·61	575·05	574·08	61	5·97	535·25	531·69
30	1·97	569·17	567·99	62	6·17	534·22	530·55
32	2·13	566·85	565·58	63	6 38	533·20	529·42
35	2·39	563·42	561·99	64	6·59	532·18	528·28
				65	6·81	531·17	527·14
40	2·86	557·77	556·03	66	7·04	530·16	526·01
41	2·97	556·66	554·86	67	7·27	529·15	524·86
42	3·08	555·55	553·69	68	7·51	528·14	523·71
43	3·20	554·44	552·52	69	7·76	527·14	522·56
44	3·32	553·34	551·35	70	8·01	526·15	521·41
45	3·44	552·24	550·19	71	8·27	525·16	520·27
46	3·56	551·15	549·02	72	8·54	524·17	519·12
47	3·69	550·06	547·85	73	8·82	523·18	517·98
48	3·82	548·97	546·69	74	9·10	522·20	516·83
49	3·96	547·89	545·53	75	9·39	521·22	515·69
50	4·10	546·81	544·37				
51	4·24	545·74	543·21	80	10·98	516·39	509·97
52	4·39	544·67	542·06	85	12·78	511·65	504·19
53	4·55	543·61	540·89	90	14·85	506·99	498·43
54	4·71	542·55	539·75	95	17·18	502·41	492·56
55	4·87	541·50	538·60	100	19·84	497·93	486·65

Thus one cubic foot of dry air, after becoming saturated with moisture, expands into the volume $\dfrac{1}{1-\dfrac{E_t}{p}}$ if it be confined under the same pressure as before.

We may now find the weight of a cubic foot of air saturated with aqueous vapour at any temperature: for it is obviously

$$(\text{Weight of cubic foot of dry air} + \text{weight of cubic foot of vapour}) \times \frac{p-E_t}{p}.$$

Thus are obtained the numbers in column 4 of Table III. When the dry- and wet-bulb thermometers read alike, we have at once the weight of a cubic foot of the atmosphere for the barometric pressure of 30 inches. For any other height of the barometer we must multiply by this height in inches and divide by 30. When the air is not saturated, we must subtract the following:

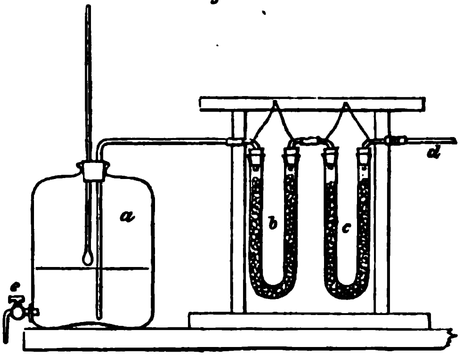
$$\left(\begin{matrix}\text{Weight of cub.}\\ \text{ft. of dry air}\end{matrix}\right\} - \left\{\begin{matrix}\text{weight of cub. ft.}\\ \text{of saturated air}\end{matrix}\right) \times \frac{\text{Weight of cubic foot of vapour at dew-point}}{\text{Weight of cubic foot of vapour at temperature of air}}:$$

from the weight of a cubic foot of dry air, and reduce the result as before to the barometric pressure at the time.

The Degree of Humidity represents the proportional saturation of the air with moisture, decimally expressed, so that saturated air has the degree 100, and perfectly dry air the degree 0. It is found by dividing the weight of vapour (Table III. column 2) at the dew-point by the weight which would be present at the temperature of the air, if it were saturated. Some writers use the corresponding elastic forces of the vapours at the dew-point and temperature of the air (Table II.) in place of the weights of vapour, but the results are nearly the same.

Chemical Method of Hygrometry. The chemist may always avoid the difficulties attending the use of hygrometers, by absorbing the aqueous vapour from any given volume of air and actually weighing it upon the chemical balance. The necessary apparatus (*fig.* 571) consists of a common aspirator *a* and two U-shaped drying tubes *b*, *c*, containing fragments of pumice-stone soaked in strong sulphuric acid. The aspirator being full of water, the second tube *c* is detached, weighed accurately, and again attached on one side to the other drying tube *b*, on the other side to a long *perfectly dry* tube *d*, by means of which air from any required point, as for instance from the open atmosphere outside the laboratory window, may be drawn through the apparatus.

Fig. 571.



The fixed drying tube *b* is employed to prevent any vapour passing back from the aspirator. Regnault took great pains to ascertain the least necessary size of the weighed drying tube. He generally indeed employed two weighed tubes, each 0·18 metre in height, filled with *large* fragments of pumice-stone. But the second tube *rarely* gained 1 or 2 milligrammes in weight, and chiefly served to afford a proof that the absorption by the first tube was complete. It is probably best therefore to dispense with a second weighed tube, as the increased error in weighing the larger apparatus will probably be greater than the minute weight of vapour which may be lost. Additional accuracy may always be had by increasing the volume of air passed through the tube.

A determinate volume of water having been allowed to flow slowly and uniformly from the aspirator by the tap *e*, an equal volume of air, of course, passes through the tube *c*, and becomes desiccated. The weight of vapour absorbed is learnt by again weighing the tube *c*, but to determine the corresponding weight of air with accuracy, we must read the temperature at the end of the experiment by a thermometer placed in the centre of the aspirator, and likewise observe the barometer, then performing the calculation as directed on page 230.

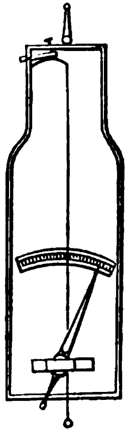
This method may also be used to determine the amount of water *suspended* in the air in the form of mist or cloud. The weight of the watery particles is the excess of the whole weight absorbed over the maximum weight of vapour (saturated) as given in Table III. column 2.

The chemical determination of vapour has been fully considered by **Brunner.** (Ann. Ch. Phys. [3] iii. 309.)

The chemical method might obviously be used to determine the average amount of vapour in the air during any period of time. It is only necessary for this purpose that a perfectly uniform stream of air pass through the drying tube throughout the period. The total weight of vapour absorbed, divided by the total weight of air passed through, gives the required result. Such a process was proposed by Dr. **Andrews** (Brit. Assoc. 1851, Trans. of Sec. p. 29), who has also described an aspirator suitable for the purpose (Phil. Mag. [4] iv. 330), and we know not why it is not adopted, at least in some of the principal observatories.

Hygroscopic bodies. Most organised structures expand or contract according to their state of moisture or dryness, and many organic substances to such a degree that they afford very delicate indications of hygrometric changes. Thus a thin shaving of whalebone laid on the hand instantly curls up, and a slip of whalebone furnished with a multiplying index formed the hygrometer finally adopted by **Deluc** (Phil. Trans. [1791] lxxxi. 419). An ivory hygrometer was also constructed by **Deluc** (Phil. Trans. [1773] p. 404) and **Leslie** (Ann. Ch. Ph. i. 468). A hygroscope formed of pieces of deal-wood was designed in 1676 by **John Coniers** (Phil. Trans. xi. 715). Chimney ornaments are often seen in which certain figures are caused to move by the contraction or expansion of catgut, thus indicating the approach of rain or fine weather. The awn of the *Andropogon contortum* has been used for similar purposes by Capt. **Kater**; the awn of the *Avena fatua*, or wild oat, by **Hooke**; the internal membrane of the *Arundo Phragmites*, or common reed, by **Adie**; and the *Funaria hygrometrica*, or common cord-moss, the arista of the seed of the *Stipa pennita*, or common feather-grass, by others. The hygroscope usually placed at the top of the common barometer or weather-glass consists of an awn or vegetable filament which in twisting or untwisting moves a light index.

Fig. 572.



Saussure's Hair Hygrometer is the only instrument of this class which has been supposed in late years to possess any scientific accuracy or importance. To construct it, long, soft and straight human hairs must be procured and boiled for half an hour in a litre of water containing 10 grammes of crystallised carbonate of soda. After being well washed in pure water and dried without heat, the best hair is chosen, of a length of about 24 centimetres. One end is fixed to the top of the instrument (*fig.* 572), and the other, being passed round a pulley of the diameter of 5 millimetres, is attached to a weight of about 0·2 gramme (3 grains). An index fixed to the pulley moves over a divided circle, the divisions of which are determined by placing the instrument first over water and then over sulphuric acid, that is in perfectly moist and perfectly dry air, and dividing the space which the index is thus caused to move over into 100 equal parts. When well and delicately constructed, such an instrument will promptly show the slightest changes of moisture in the air.

Regnault, in his "Etudes de l'Hygrométrie," has spent much labour and ingenuity in trying to render the Hair Hygrometer scientifically useful. He has only succeeded in showing that two of these instruments will give very different results, if there exists the slightest difference in the nature of the hairs, their preparation, or the weight by which they are extended; that the most carefully constructed instruments are but little accordant; and that, after all, the degrees are quite arbitrary, and can only be reduced to true degrees of humidity or force of aqueous vapour, by a table specially determined by experiment for each instrument. Such a table may be found in Pouillet's *Elements de Physique*, 7th ed. ii. p. 742, having been prepared by Gay-Lussac, and supposed by him to apply to all Hair Hygrometers.

Regnault, indeed, has found that the zero of the Hair Hygrometer, at which it should stand in perfectly dry air, is quite illusory, for the hair will continue to shrink more or less even when it has been exposed for some months to the dry air. He therefore commences the graduation for air about ⅕ saturated, or of 20 degrees of humidity.

Kæmtz (*Météorologie*, Paris, 1858, p. 74) compares the table of Gay-Lussac with others calculated for Saussure's Hygrometer by Prinsep, Melloni, and August. There is very little accordance.

A great number of experiments on hygroscopes and hygroscopic substances are given in the three elaborate papers by Deluc in the Philosophical Transactions (1773 and 1791), and he says (Ph. Trans. [1791] lxxxi. 40), "I have concentrated in these pages an account of twenty years' assiduous labours in *hygrometry*, mostly occasioned by the anomalies of the *hygroscopic threads*."

There is a complete and learned history of hygrometry by Suerman, entitled "Commentatio de definiendâ Quantitate Vaporis aquei in Atmospherâ," 4to. Lugd. Bat. 1831.

In Prof. Forbes' *Supplementary Report on Meteorology* (Brit. Assoc. Report, 1840. pp. 95–101) is an excellent *résumé* of the theory of the wet-bulb thermometer.

A general account of hygrometry, with examples of the calculations required in meteorology, is to be found in Dr. Drew's *Practical Meteorology*. W. S. J.

HYOCHOLALIC ACID. Syn. with Hyocholic Acid.

HYOCHOLIC ACID. $C^{25}H^{40}O^4$.—An acid obtained, together with glycocine, by the action of potash on hyoglycocholic acid. It is insoluble in water, soluble in alcohol and ether, and crystallises in mammellated granules. Its *barium-salt* dried at 180° contains $C^{25}H^{39}BaO^4$. (Strecker.)

HYOGLYCOCHOLIC ACID. $C^{27}H^{43}NO^5$. Formerly called *Hyocholic acid.* (Strecker and Gundelach, Ann. Ch. Pharm. lxii. 205.)—An acid which, in the form of a sodium-salt, constitutes the principal parts of the bile of the pig: hence its name (from ὗς, ὑός a pig, and χολή bile).

To prepare the sodium-salt in the pure state, the fresh bile is completely saturated with sulphate of sodium; the mixture is heated for some hours on a sand-bath, and then left to cool; and the resulting precipitate, consisting of hyoglycocholate of sodium mixed with mucus and a small quantity of yellow colouring matter, is washed with a concentrated solution of sulphate of sodium, first by decantation and then on a filter, after which it is dried at 110° C. and treated with absolute alcohol, which dissolves the hyoglycocholate of sodium. The alcoholic solution is decolorised with animal charcoal, then precipitated by ether, and the precipitate is dried at 100°.

The free acid is obtained by precipitating the aqueous solution of the sodium-salt with dilute sulphuric acid, dissolving the precipitate in alcohol and precipitating with water. The liquid is milky at first, but becomes limpid after a while, and deposits transparent drops. It must be left on the sand-bath for several days, because the precipitation is not complete till the last traces of alcohol are evaporated. By repeating this operation two or three times, the acid is obtained quite pure.

Hyoglycocholic acid is a white resinous body which melts in hot water, and then presents a silky aspect. It solidifies after remaining for a few days over the water-bath, and after it has lost all traces of water; does not melt even at 120°. It is but slightly soluble in water, imparting, however, an acid reaction; easily soluble in *alcohol*, but quite insoluble in *ether*. It dissolves readily in *ammonia* and in dilute solutions of the *fixed alkalis* or their *carbonates*. According to F. Hoppe (Jahresber. 1858, p. 568), the solutions of the free acid exhibit an optical rotatory power = + 2°; that of the sodium-salt does not act on polarised light. It differs from the acid of ox-bile (glycocholic acid) by its sparing solubility in water, and by forming precipitates insoluble in water, with baryta, lime, &c.; in this respect it resembles cholonic and choloïdic acids.

Hyoglycocholic acid is not altered by dilute *sulphuric acid:* the concentrated acid blackens it, with evolution of sulphurous acid. It is not oxidised by a mixture of *sulphuric acid and peroxide of lead;* but when the acid or any of its salts is heated with concentrated *nitric acid*, nitrous fumes are evolved, and a yellowish mass is formed, consisting chiefly of oxalic and cholesteric acids; at the same time volatile fatty acids are formed homologous with acetic acid. These volatile acids are also produced, together with hydrocyanic acid, when hyoglycocholic is oxidised by a mixture of *chromate of potassium and sulphuric acid.*

Hyoglycocholic acid, boiled for a long time with strong *hydrochloric acid*, is decomposed in the same manner as glycocholic acid (ii. 900), yielding first a resinous substance soluble in alkalis (hyocholoïdic acid ?), then hyodyslysin insoluble in alkalis, while glycocine remains in solution:

$$\underset{\text{Hyoglycocholic acid.}}{C^{27}H^{43}NO^{5}} = \underset{\text{Hyodyslysin.}}{C^{25}H^{36}O^{3}} + \underset{\text{Glycocine.}}{C^{2}H^{5}NO^{2}}$$

Potash induces a similar transformation, yielding hyocholic acid, which differs from hyodyslysin only by the elements of 1 at. water.

Hyoglycocholic acid is monobasic, the *hyoglycocholates* in the dry state containing $C^{27}H^{42}MNO^{5}$. The *ammonium-salt* is obtained by adding chloride, carbonate, or sulphide of ammonium to fresh pig's bile, or a solution of the sodium-salt. It dissolves very easily in water, but very sparingly in strong solutions of ammoniacal-salts. It is decomposed by boiling. The *barium-salt*, $2C^{27}H^{42}BaNO^{5}.H^{2}O$, dissolves very sparingly in water, very readily in alcohol. The *calcium-salt*, $2C^{27}H^{42}CaNO^{5}.H^{2}O$, resembles the barium-salt. The *lead-salt* is a white precipitate obtained by mixing a solution of the sodium-salt with neutral acetate of lead. This mother-liquor yields with the basic acetate another precipitate which appears to be a basic salt.

The *potassium-salt*, $2C^{27}H^{42}KNO^{5}.H^{2}O$, is prepared by dissolving the acid in caustic potash, and treating the solution with sulphate of potassium, &c., as in the preparation of the sodium-salt. It is a white amorphous mass, which melts at the heat of the water-bath so long as it retains water or alcohol; when quite dry, it remains solid even at 120°.

The *silver-salt*, $C^{27}H^{42}AgNO^{5}$, is a gelatinous precipitate, which becomes flocculent when boiled.

The *sodium-salt*, $2C^{27}H^{42}NaNO^{5}.H^{2}O$, is a white powder which does not become moist by exposure to the air. Its alcoholic solution yields by evaporation a perfectly transparent varnish. It has a bitter and very persistent taste. Heated on platinum-foil, it melts, swells up, and burns with a smoky flame.

HYOCHOLOÏDIC ACID. The resinous substance formed previous to hyodyslysin, when hyoglycocholic acid is boiled with strong hydrochloric acid, is perhaps homologous with choloïdic acid, $C^{24}H^{38}O^{4}$. According to Hoppe (Jahresber. 1858, p. 568), its solutions have a dextro-rotatory power = 23·6°.

HYODYSLYSIN. $C^{25}H^{36}O^{3}$.—A substance homologous with dyslysin, produced by the continued action of boiling hydrochloric acid on hyoglycocholic acid. It is insoluble in water, potash, and ammonia, sparingly soluble in boiling alcohol, moderately soluble in ether.

HYOSCYAMINE. (Geiger and Hesse, [1833] Ann. Ch. Pharm. vii. 270.)—An alkaloïd contained in henbane (*Hyoscyamus niger*), and other species of Hyoscyamus. To prepare it, the bruised seeds of henbane are exhausted with hot alcohol containing 2 per cent. of sulphuric acid; the expressed juice is mixed with a quantity of slaked lime, sufficient to produce a strong alkaline reaction; the filtered liquid is slightly supersaturated with sulphuric acid, and again filtered; the alcohol is distilled off to one-fourth; the residue diluted with water; and the rest of the alcohol driven off at the lowest possible temperature. To the remaining liquid is then cautiously added a concentrated solution of carbonate of potassium, the liquid being again filtered if any turbidity is thereby produced; then a large excess of the same solution; and the whole is shaken with ether as long as that liquid takes anything up. The ethereal solution, separated from the watery liquid and evaporated, leaves impure hyoscyamine, which may be purified by mixing it with water till a clear solution is produced; adding to this solution twice its weight of ether-alcohol, digesting with animal charcoal, and evaporating off the ether-alcohol, first at a gentle heat, and afterwards in vacuo. If the residue is still coloured, it must be once more dissolved in dilute acid; the solution mixed with an equal quantity of alcohol, digested with animal charcoal, and decomposed by excess of carbonate of potassium; the hyoscyamine extracted by ether; and the whole process repeated if necessary.

Hyoscyamine may also be prepared, though less advantageously, from the herb of the plant, while in flower, by boiling the expressed juice, filtering, mixing with lime, treating the filtrate with excess of carbonate of potassium, and dissolving out the hyoscyamine by agitation with ether. The dried herb likewise yields it when treated with acidulated alcohol.

Hyoscyamine crystallises in stellate groups of silky needles, but is frequently also obtained as an amorphous sticky mass. When perfectly dry it is inodorous, but in the moist state, it has an unpleasant odour resembling that of tobacco. It is soluble in *water*, *alcohol*, and *ether*. The aqueous solution has an alkaline reaction. It melts when heated, and then volatilises with partial decomposition. It is decomposed when heated with *acids*. Strong *nitric acid* dissolves it without colour; strong *sulphuric acid* turns it brown. *Iodine* added to its aqueous solution forms a copious precipitate having the colour of kermes. Taken internally, even in small doses, it acts as a narcotic poison. Rubbed into the eye, even in minute quantity, it produces persistent dilatation of the pupil.

Hyoscyamine neutralises acids completely. Many of its salts crystallise and are permanent in the air. They have no odour, but an acrid, nauseous taste, and are very poisonous. Their solutions are not precipitated by dichloride of platinum; but yield whitish flocks with chloride of gold. With infusion of galls they form a white precipitate.

HYPARGYRITE. See MIARGYRITE.

HYPERSPIROÏLIC ACID. Syn. with SALICYLIC ACID.

HYPER, as a prefix, syn. with PER.

HYPERSTHENE (from *ὑπέρ* and *σθένος*, strength, on account of the greater hardness and density of this mineral as compared with hornblende, with which it was formerly confounded). It is a sub-species of augite, containing, according to **Muir's** analyses (Pogg. Ann. lxiv. 162),

SiO^2	Al^4O^3	Ca^2O	Mg^2O	Fe^2O	Mn^2O	H^2O	
51·35	. .	1·83	11·09	33·92	. .	0·50	= 98·69

It is distinguished from common augite and diallage by its small proportion of calcium and large proportion of iron, and may be represented by the formula $(Mg\,;\,Fe)^2SiO^3$.

Hypersthene has a density of 3·3—3·6, and a greyish or greenish-black colour, with a more or less distinct copper-red metallic iridescence on the most distinct cleavage-surface, arising from the presence of microscopic laminæ of titaniferous iron imbedded in the mineral. It is remarkable that all the augitic rocks of Sweden contain titaniferous iron.

The name *Paulite* is given to hypersthene found in the island of St. Paul on the coast of Labrador. *Gedrite* is hypersthene in which the quantity of iron attains its maximum.

HYPERSTHENITE or *Hypersthene-rock* is a crystallo-granular mixture of hypersthene and labrador, with small quantities of titaniferous iron imbedded in the hypersthene, and occasional admixture of iron pyrites, mica, hornblende, olivine, garnet, opalite, &c. Labrador is usually the chief component. Quartz is never found in this rock. Hypersthene-rock belongs to the less frequently occurring crystalline, unstratified formations. It is found in the island of St. Paul, on the coast of Labrador, at Elfdalen in Sweden, at several localities in Norway, in the Isle of Skye, in Cornwall, in the Harz in Silesia, Bohemia, &c.

The following analyses of hypersthenite are by **Bunsen** (Jahresb. 1861, p. 1070): *a.* Coarse-grained, containing brown hypersthene and greyish-white labradorite, from a vein near Penig in Saxony.—*b.* Medium-grained, greenish-brown, containing greenish-white labradorite and dark green augite, from Tabor, near Getschin in Bohemia.—*c.* Somewhat finer-grained and browner, from Stransko near Liebstadl.—*d.* Greyish-green, crystalline, medium-grained, very slightly magnetic, containing triclinic felspar, from Hrabacow near Starkenbach.—*e.* From the railway cutting of the Woleschka valley, between Semil and Kostialow near Poric. It is finely crystalline, dark grey to greenish, and effervesces with acids, in consequence of small masses of calcspar disseminated through it; scarcely magnetic, and with a weathered crust:

	SiO^2	Al^4O^3	Fe^4O^3	Ca^2O	Mg^2O	K^2O	Na^2O	H^2O	
a.	49·90	16·04	7·81	14·49	10·08	0·55	1·68	1·46	= 102·01
b.	49·97								
c.	56·20	15·26	13·40	9·50	3·21				
d.	51·98	16·27	13·53	7·34	5·85	3·30	1·20	2·71	= 102·18
e.	54·44	18·06	9·64						

HYPOBROMOUS ACID. BrHO.—The formation of bleaching liquids analogous to the hypochlorites by the action of bromine on solutions of the alkalis and alkaline earths was noticed by Balard in his original memoir on bromine (Ann. Ch. Phys. [2] xxxii. 337), and subsequently by Löwig (Pogg. Ann. xiv. 14, 485), Fritzsche (J. pr. Chem. xxiv. 294), and Gay-Lussac (Compt. rend. xiv. 951). Balard also found that bromine-water forms with mercuric oxide a sparingly soluble oxybromide of mercury and a bleaching liquid which, by distillation in a vacuum, yields a liquid also possessing bleaching properties, and supposed to be hypobromous acid (i. 679).

More recently, Spiller (Jahresber. 1859, 97; 1862, 73) and Dancer (Chem. Soc. J. xv. 447) have shown that when bromine is added to excess of solution of nitrate of silver, half the bromine is precipitated as bromide of silver, while the other half remains in solution as hypobromous acid, forming a strongly bleaching liquid, from which, according to Dancer, the hypobromous acid may be distilled under a pressure of 50 mm. of mercury, the liquid then boiling at 50°. The distillate, which does not contain free bromine, is straw-yellow, has an acid reaction, bleaches strongly, and decomposes when heated above 60°. It gave by analysis numbers corresponding with the formula of hypobromous acid.

Hypobromous acid is likewise obtained in solution by agitating bromine-water with excess of mercuric oxide or oxide of silver. When bromine is brought in contact with excess of dry mercuric oxide, the mixture becomes very hot. By heating the two substances together in a sealed tube to 100° a powder is obtained which smells like chloride of lime and bleaches when moistened with water; it is a mixture of mercuric bromide, oxide and hypobromite. If the bromine is in excess, a solid mass is formed consisting merely of mercuric bromide and oxide. Oxygen is set free in both cases. (Dancer.)

All attempts to prepare hypobromous anhydride by methods similar to those which yield hypochlorous anhydride (i. 908) were unsuccessful, the compound being decomposed, both at common temperatures and at −18°, into bromine and oxygen.

HYPOCHLORIC ACID. Syn. with Perchloric oxide. (See CHLORINE, OXIDES OF, i. 912.)

HYPOCHLORITE. (*Grüne Eisenerde.*)—A mineral occurring at Schneeberg, Johanngeorgenstadt, and Bräunsdorf in Saxony, in minute greenish crystals and grains, or massive and earthy. It contains, according to Schüler's analysis, 50·24 per cent. silica, 14·65 alumina, 13·03 oxide of bismuth, 10·54 protoxide of iron, and 9·62 phosphoric anhydride, with a trace of manganese, and is perhaps a silicate of bismuth and iron mixed with phosphate of aluminium. (Dana, ii. 182.)

HYPOCHLORITES. ClMO.—The formation, general properties and reactions of these salts, and the methods of estimating the quantity of available chlorine contained in them, have been already described under CHLORINE (i. 904, 908). For the preparation of hypochlorite of calcium, its uses as a bleaching and disinfecting agent, and the methods of estimating its commercial value, see *Ure's Dictionary of Arts*, &c. i. 904; also *Richardson and Watts's Chemical Technology*, vol. i. pt. 3, pp. 360–425.

A sample of "chloride of lime," analysed by F. Rose under the direction of Fresenius (Ann. Ch. Pharm. cxviii. 317), yielded 26·72 per cent. CaClO, 25·51 CaCl, 23·05 Ca^2O, and 24·72 combined and hygroscopic water. On repeatedly triturating it with fresh quantities of water to a thin pulp, the chloride of calcium was found to dissolve at the first trituration, the hypochlorite only at the third. Hence Fresenius concludes that the two salts exist in the bleaching powder merely in a state of mixture, or at most as a loose combination easily decomposed by water. He regards bleaching powder as a mixture of hypochlorite and basic chloride or oxychloride of calcium, $CaClO + (CaCl.Ca^2O).2H^2O$. The basic chloride is resolved by water into chloride and hydrate of calcium.

Solutions of the hypochlorites of the alkali-metals have long been used as disinfecting agents. The so-called chloride of soda or Labarraque's disinfecting liquid, is a mixture of hypochlorite and chloride of sodium, prepared by passing chlorine into a solution of caustic soda or carbonate of sodium, or by decomposing hypochlorite of calcium (bleaching powder) with carbonate or sulphate of sodium. In the first mode of preparation, about 40 lbs. of soda-crystals are dissolved in about 20 gallons of water, and a stream of chlorine is passed through the solution till it has attained a specific gravity of 1·06. A rise of the density above this point indicates the formation of chlorate of sodium. To prepare the disinfecting liquid by the second method, about 20 lbs. of good bleaching powder are dissolved in about 26 gallons of water, and to the filtered liquid is added a solution of 40 lbs. soda-crystals in about 9 gallons of warm water. The filtered solution constitutes Labarraque's liquid.

Chloride of Potash or *Eau de Javelle* is a mixture of hypochlorite and chloride of potassium prepared by similar methods.

A mixture of *hypochlorite of magnesium*, prepared by decomposing chloride of lime with an equivalent quantity of sulphate of magnesium, is said by Claussen to be more efficacious than other chlorine-compounds for bleaching flax and hemp.

Hypochlorite of Aluminium, prepared by mixing equivalent quantities of sulphate of aluminium and hypochlorite of calcium, is recommended by Orioli (Rep. Pat. Inv. April 1860) as a bleaching and antiseptic agent. It is very easily decomposed, and therefore acts very rapidly on organic matters. It may also be used as a mordant instead of acetate of aluminium, all the hypochlorous acid being disengaged at the heat of the dye-bath while the alumina remains attached to the fibre.

Hypochlorite of Zinc is also used as a mordant, and is recommended by Varrentrapp (Dingl. pol. J. clviii. 378), on account of its ready decomposibility, as a bleaching agent. The action of chloride of lime may be advantageously accelerated by the addition of chloride of zinc instead of a mineral acid.

HYPOCHLOROUS ACID and **ANHYDRIDE** (i. 908).—This gas is absorbed by sulphuric anhydride, and when the latter compound, in a state of perfect dryness and in quantities of not more than 5 or 6 grms. at a time, is saturated with hypochlorous anhydride, a dark-red thickish liquid is formed, which solidifies on cooling to a mass of light red needles apparently consisting of $Cl^2O.4SO^3$. These crystals melt at 55°, and detonate when suddenly raised to a higher temperature. They are instantly decomposed by water into sulphuric and hypochlorous acids; hence the compound acts as a powerful oxidising agent on sugar, alcohol, and other organic substances. Iodine decomposes it, with evolution of chlorine and formation of iodic acid.

When hypochlorous anhydride is passed into liquid sulphurous anhydride, a very brisk reaction takes place as soon as the containing vessel is removed from the freezing mixture, chlorine being evolved and a red viscid substance remaining, composed of sulphuric and hypochlorous anhydrides in a proportion not yet determined. (Schützenberger, Compt. rend. lii. 135; liii. 538; Jahresber. 1861, p. 142.)

HYPOGÆIC ACID. $C^{16}H^{30}O^2 = \left.\begin{matrix}C^{16}H^{29}O\\H\end{matrix}\right\}O$.—An acid belonging to the oleic series $C^nH^{2n-2}O^2$, discovered in 1855 by Gössmann and Scheven (Ann. Ch. Pharm. xciv. 230) in oil of earthnut (*Arachis hypogæa*) It is isomeric, if not identical, with physetoleic acid, discovered in 1844 by Hofstädter (Ann. Ch. Pharm. xci. 177) in sperm-oil (see PHYSETOLEIC ACID), also with the acid obtained by oxidation of axinic acid ($C^{18}H^{28}O^2$), an acid produced by the saponification of the fatty substance, age or axin, contained in the Mexican plant, *Coccus Axin*. (F. Hoppe, J. pr. Chem. lxxx. 102.)

Preparation from Earth-nut oil.—The fatty acids of the oil are dissolved in alcohol; arachidic and palmitic acids are precipitated by ammonia and acetate of magnesium; the precipitate is removed; and the filtrate is mixed with ammonia and an alcoholic solution of neutral acetate of lead. The precipitate is collected after a few days, pressed and dissolved in ether; the ethereal solution is agitated with aqueous hydrochloric acid; the chloride of lead is filtered off; the filtrate is shaken up with water which has been freed from air by boiling; the ethereal layer which separates again on leaving the liquid at rest is taken off; and the ether is removed by distillation. The remaining liquid on cooling deposits yellowish crystals, which may be purified by pressure and recrystallisation from alcohol at a very low temperature. An additional quantity of crystals may be obtained from the mother-liquor. (Gössmann and Scheven.)

Axinic acid yields by oxidation, aginin insoluble in ether, and the acid, $C^{16}H^{30}O^2$, which may be dissolved out by ether, and crystallises from the ethereal solution.

Hypogæic acid crystallises in stellate groups of needles, inodorous, melting at 34° or 35° (physetoleic acid melts at 30° and solidifies at 28°), easily soluble in alcohol and in ether.—1. When exposed to the air, it acquires a yellowish colour and rancid odour, and then crystallises with difficulty, even at very low temperatures.—2. When subjected to dry distillation, it first gives off a reddish-yellow liquid, then yellowish-white crystalline sebacic acid, and lastly, a fetid oil, leaving a small quantity of charcoal.

Nitrous acid converts hypogæic acid into the isomeric compound gaïdic acid, which is related to it in the same manner as elaïdic to oleic acid. It forms a colourless crystalline mass, permanent in the air, melting at 38°, solidifying in the radio-crystalline form on cooling, and volatilising undecomposed at higher temperatures. (Caldwell and Gössmann, Ann. Ch. Pharm. xcix. 305.)

Hypogæic acid is monobasic. The *barium-salt* is obtained by adding alcoholic acetate of barium to an alcoholic solution of the acid mixed with excess of ammonia, in white grains which dissolve when heated and separate again on cooling.

Hypogæate of Copper, $C^{16}H^{29}CuO^2$, is obtained, in like manner, by mixing alcoholic cupric acetate with a hot alcoholic solution of the acid containing ammonia, and separates on cooling in violet-blue crystalline grains, soluble in alcohol and cohering to a translucent wax at 75°.—*Gaïdate of copper* is obtained by mixing aqueous gaïdate of sodium with cupric sulphate, as a scarcely crystalline precipitate, which dissolves with difficulty in alcohol, and separates therefrom in granules. It melts without decomposition at a temperature above 120°.

Hypogæate of Ethyl, $C^{16}H^{29}(C^2H^5)O^2$, is obtained by passing hydrochloric acid gas through a solution of hypogæic acid in alcohol of 95 per cent. and separates on warming the liquid, as an oil which may be freed from adhering acid by washing with small quantities of alcohol, and dried in a stream of carbonic anhydride between 100° and 120°. It is yellow, inodorous, lighter than water, but sinks in alcohol, in which it is but slightly soluble. Not volatile without decomposition.

Gaïdate of Ethyl is prepared by passing hydrochloric acid gas through a solution of gaïdic acid in absolute alcohol, precipitating after 12 hours with water, and subjecting the separated mixture of gaïdic ether and gaïdic acid to a second treatment with hydrochloric acid. The product is washed and dried at 100° in a stream of hydrogen. It is a colourless, lamino-crystalline mass, which melts between 9° and 10°, and volatilises undecomposed at a higher temperature. It is inodorous, lighter than water, heavier than alcohol, and sparingly soluble in alcohol.

Gaïdate of Silver is obtained by precipitation as a white amorphous mass which, when washed, and especially if heated with water, alcohol or ether, turns black without dissolving.

Gaïdate of Sodium is obtained by dissolving the acid in aqueous carbonate of sodium, evaporating, and exhausting the residue with absolute alcohol; the solution on cooling deposits the salt as a translucent jelly: from dilute solutions it separates in crystalline grains.

HYPOGALLIC ACID. $C^7H^6O^4$. (Matthiessen and Foster, Chem. Soc. J. xvi. 350.)—An acid produced by the action of boiling concentrated hydriodic acid on hemipinic acid (p. 142):

$$\underset{\text{Hemipinic acid.}}{C^{10}H^{10}O^6} + 2HI = \underset{\text{Hypogallic acid.}}{C^7H^6O^4} + \underset{\text{Iodide of methyl.}}{2CH^3I} + CO^2.$$

It is isomeric with carbohydroquinonic, protocatechuic and oxysalicylic acids, and intermediate in composition between salicylic acid, $C^7H^6O^3$, and gallic acid, $C^7H^6O^5$.

Hypogallic acid, when pure, is only slightly soluble in cold water, but dissolves easily in hot water, alcohol, and ether; its solution reacts strongly acid with litmus-paper. It separates from hot water in small prismatic crystals, united into stellate groups, and containing 1½ at. water of crystallisation, which they lose at 100°. The acid melts at about 180°, but as it begins to decompose even at a lower temperature, its melting-point could not be accurately ascertained.

Hypogallic acid gradually turns brown when heated in the air to a little above 100°; the same change occurs more quickly when a solution of it, especially if neutral or alkaline, is evaporated. Added to solution of *nitrate* or *ammonio-nitrate of silver*, it causes an immediate precipitation of metallic silver, even in the cold; with *sulphate of copper* and a slight excess of potash, it gives a yellowish green solution, from which an orange-yellow precipitate is thrown down on warming; in a mixture of *sesquichloride of iron and red prussiate of potash*, it immediately produces a blue precipitate; when boiled with solution of *mercuric chloride*, it reduces it to calomel. With *sesquichloride of iron*, it gives an intense indigo-blue coloration, which is changed to violet by a very small quantity of ammonia, and to blood-red by excess of ammonia, no precipitate being produced, unless too much chloride of iron has been used; the colour is destroyed by strong acids, but restored by neutralisation with alkali, and partially by addition of water. A solution of the acid immediately becomes brown on addition of *alkali*, the colour quickly becoming darker by exposure to the air. With *ammonia and chloride of barium* or *calcium*, it gives a brownish white flocculent precipitate; with *acetate of lead*, a pale yellow precipitate.

Hypogallic acid is decomposed by heat into carbonic anhydride and a substance which solidifies in the neck of the retort to a colourless crystalline mass. The decomposition begins at about 170°, and goes on rapidly at 200°. The crystalline product melts, in the crude state, at about 90°; it dissolves easily in water, and crystallises in needles when the solution is evaporated. It is rapidly attacked by nitric acid, even when diluted, giving a red-brown solution. With sesquichloride of iron it gives a bluish-black amorphous precipitate; with acetate of lead it gives a white or yellowish-white precipitate, soluble in an excess of acetic acid. It slowly assumes a darker colour by exposure to air in contact with alkali. This substance has not yet been prepared in sufficient quantity for complete investigation.

The three acids above mentioned as isomeric with hypogallic acid, have about the same solubility in water, alcohol, and ether, as the latter; they all likewise give a dark coloration with the smallest trace of sesquichloride of iron; reduce nitrate of silver; become dark brown when mixed with alkali and exposed to the air; give a yellowish-white precipitate with acetate of lead; and at a high temperature are all decomposed into carbonic anhydride and oxyphenic acid or hydroquinone. Nevertheless, no two of these acids appear to have quite the same properties. The following are the most important points in which differences have been observed. Hypogallic acid crystallises with 1½ molecule of water (14·9 per cent.), carbohydroquinonic and protocatechuic acids with 1 molecule (10·4 per cent.), and oxysalicylic acid without water. Hypogallic and oxysalicylic acids give a dark-blue colour with sesquichloride of iron, the other two acids a dark-green colour. Hypogallic acid reduces nitrate of silver immediately in the cold; carbohydroquinonic acid reduces it slowly in the cold, rapidly when boiled; oxysalicylic acid has no action on nitrate of silver in the cold, but reduces it completely when boiled. Carbohydroquinonic acid reduces cuprous oxide from a mixture of cupric acetate, tartaric acid, and excess of potash; protocatechuic acid causes no reduction of the same solution. Hypogallic acid causes a precipitate in a mixture of chloride of barium and ammonia; protocatechuic acid only on addition of alcohol. Some of these differences may perhaps be due to accidental causes, depending on the different sources and modes of preparation.

HYPO-IODIC ACID. See Iodine, Oxacids of.

HYPONIOBIC ACID. See Niobium.

HYPONITRIC ACID. Syn. with Pernitric oxide. (See Nitrogen, Oxides of.)

HYPONITROMECONIC ACID. Syn. with Nitromeconin. (See Meconin.)

HYPONITROUS ACID. Syn. with Nitrous acid.

HYPOPHOSPHOROUS ACID. See Phosphorus, Oxygen-acids of.

HYPOSCLERITE. A name applied by Breithaupt to a mineral from Arundel, which, according to Rammelsberg, is probably albite mixed with augite. (See Albite under Felspar.)

HYPOSTILBITE. Syn. with Stilbite.

HYPOSULPHAMYLIC ACID. Syn. with Amyl-sulphurous acid. (See Sulphurous ethers.)

HYPOSULPHARSENIOUS ACID. Syn. with Disulphide of Arsenic. (See Arsenic, Sulphides of, i. 386.)

HYPOSULPHETHYLIC ACID. Syn. with Ethyl-sulphurous acid. (See Sulphurous ethers.)

HYPOSULPHINDIGOTIC ACID.
HYPOSULPHOCŒRULIC ACID. } See Indigo-sulphuric acids.

HYPOSULPHOGLUTIC ACID. Syn. with Sulphoglutic acid.

HYPOSULPHOMETHYLIC ACID. Syn. with Methyl-sulphurous acid. (See Sulphurous ethers.)

HYPOSULPHONAPHTHALIC and **HYPOSULPHONAPHTHINIC ACIDS.** See Sulphonaphthalic acids.

HYPOSULPHOPHOSPHORIC and **HYPOSULPHOPHOSPHOROUS ACIDS.** See Phosphorus, Sulphides of.

HYPOSULPHURIC and **HYPOSULPHUROUS ACIDS.** See Sulphur, Oxygen-acids of.

HYPOVANADIC ACID. See Vanadium.

HYPOXANTHINE. An azotised organic substance discovered by Scherer (Ann. Ch. Pharm. lxxiii. 328) in the spleen of man and in the ox, and since found to exist in many other parts of the animal body. It is probably identical with Sarcine (*q.v.*)

HYSSOPINE. A doubtful alkaloïd, said by Herberger to exist in the herb of *Hyssopus officinalis*.

HYSSOP, OIL OF. A volatile oil obtained from *Hyssopus officinalis* by distillation with water. It is yellow when fresh, but turns red by keeping; has a sharp taste and smells like camphor.

HYSTATITE. Syn. with Ilmenite.

I

IASPACHATES. A variety of agate.

IBERITE. A silicate from Montoval, near Toledo, occurring in large six-sided prisms with basal cleavage. Hardness = 2·5. Specific gravity = 2·89. Contains, according to Norlin (Kongl. Vetensk. Akad. Förhandlingar, 1844, 215), 40·90 per cent. SiO^2, 30·74 Al^4O^3, 15·47 Fe^2O, Mn^2O 1·33, 0·40 Ca^2O, 0·81 Mg^2O, 4·57 K^2O, 0·04 Na^2O, 5·56 H^2O = 99·82. Fuses to a dark pearl before the blowpipe. It is probably allied to dichroïte.

ICE-SPAR. A name sometimes applied to a transparent variety of felspar found in Vesuvian lavas: the term includes pellucid varieties of other species of felspar. (Dana.)

ICELAND-SPAR. Transparent calc-spar. (See Calc-Spar.)

ICHTHIDIN. A substance contained in the immature eggs of cyprinoïd fishes.

ICHTHIN. The azotised constituent of the eggs of cartilaginous fishes. It is easily extracted from the eggs of the ray by pouring the yolk into a large quantity of distilled water, washing the dense granules which fall to the bottom till the wash-water contains only traces of albumin and saline matters, and finally exhausting them with alcohol and ether.

Ichthin thus obtained forms homogeneous, white, transparent grains, soft to the touch, insoluble in water, alcohol, and ether. Hydrochloric acid dissolves it without violet coloration; it is also readily soluble in dilute acetic and phosphoric acid, and in other acids in the concentrated state. Solutions of potash and soda dissolve it slowly; ammonia does not act upon it. It gives by analysis 50·2 to 51·0 per cent. carbon, 6·7 to 7·8 hydrogen, 14·7 to 15·4 nitrogen, and 1·9 phosphorus (?). It does not appear to contain sulphur. It leaves but a trace of ash when burnt. (Valenciennes and Frémy, Compt. rend. xxxviiii. 480, 528.)

ICHTHULIN. The very young eggs of cyprinoïd fishes contain, besides icthidin, a strongly albuminous liquid which holds in suspension certain mineral salts, together with ichthulin, which may be precipitated by water. When first precipitated, it is viscid like gluten; but when treated with alcohol and ether, it loses its viscosity and becomes solid and pulverulent. Like ichthin, it dissolves in acetic and in phosphoric acid, also in hydrochloric acid, without violet coloration. It contains 52·5 to 53·3 per cent. carbon, 8·0 to 8·3 hydrogen, 15·2 nitrogen, 1·0 sulphur, and 0·6 phosphorus (?). It seems to disappear as the eggs approach maturity, and to be replaced by albumin. (Valenciennes and Frémy.)

ICHTHYOCOLL or **ISINGLASS.** See Gelatin (ii. 826).

ICHTHYOPHTHALMITE. Syn. with Apophyllite (i. 351).

ICICA-RESIN. A resin very similar to elemi, obtained from trees very common in Guiana, belonging to the order *Terebinthaceæ*. It occurs in small masses or opaque grains, having a yellowish-white colour, and a sweet, rather agreeable odour, the strength of which is increased by heat. It is friable and tasteless. It gives up nothing to water, and is but sparingly soluble in alcohol, requiring for complete solution 45 parts of cold alcohol of 36°, and 15 parts of boiling alcohol; it dissolves also in 3½ parts of oil of turpentine at ordinary temperatures. It is insoluble in alkalis. Its alcoholic solution does not precipitate lead or silver salts.

Icica-resin is composed of three distinct substances, separable by their different degrees of solubility in alcohol.

a. If the resin be completely dissolved in boiling alcohol, one of these substances, viz. brean, crystallises on cooling. It has the composition of cholesterin, and forms white, tasteless, needle-shaped crystals, insoluble in water and in alkalis, sparingly soluble in alcohol, and having a neutral reaction. It melts at 157°, and solidifies on cooling to a mass resembling amber. By dry distillation it yields empyreumatic oils, a volatile, solid, amorphous substance which collects in the neck of the retort, and a small residue of charcoal. It is dissolved, with red colour, by sulphuric acid, and precipitated unaltered by water. Nitric acid decomposes it, with evolution of nitrous fumes, forming a yellow body soluble in excess of nitric acid, and precipitated on addition of water.

b. On removing the brean and concentrating the mother-liquor, a certain quantity of the same substance, in an impure state, first separates, and afterwards another crystalline resin, **icican**, which has the same melting-point as brean, and resembles it in most of its other properties, but is distinguished by its greater solubility in alcohol. It gives by analysis 82·01 per cent. C, 11·65 H, and 6·34 O, which may be represented by the formula $C^{20}H^{34}O$. Its composition is about the same as that of the resin of *Ceroxylon Andicola.*

c. The mother-liquor of icican, after being completely freed from crystallisable matter, deposits a small quantity of a yellow amorphous resin, which melts below 100°, and is much more soluble in alcohol and ether than brean or icican. Its alcoholic solution is slightly acid to test-paper, but the resin does not dissolve in alkalis. It contains 77·93 per cent. C, 10·69 H, and 11·47 O, corresponding approximately with the formula $C^{20}H^{30}O^2$. (Scribe, Ann. Ch. Phys. [3] xiii. 166.)

IDIOTYPE. A term applied by Guthrie (Chem. Soc. J. xiii. 35) to bodies derived by replacement from the same substance, including the typical substance itself; ammonia, for example, is idiotypic with ethylamine, phenylamine, and all the organic basis derived from it by substitution, and these are idiotypic one with the other.

The same term was applied by Wackenroder (J. pr. Chem. xxiv. 18) to certain non-crystalline organic bodies which, according to his observations, exhibit certain similarities of structure.

IDOCRASE. See VESUVIAN.

IDRIALIN. $C^{42}H^{28}O$ (?).—The essential constituent of idrialite, from which it is obtained either by dry distillation in an atmosphere of carbonic anhydride—or better, by boiling the mineral with rock-oil or oil of turpentine; the liquid on cooling solidifies in a mass, which may be freed from the solvent by means of bibulous paper.

Idrialin forms colourless scales, which melt at a very high temperature, with partial decomposition. When distilled, it partly volatilises, but at least $\frac{9}{10}$ of it is decomposed at the same time, even in an atmosphere of carbonic anhydride. It is insoluble in *water*, even at the boiling heat, and nearly insoluble in *alcohol* and *ether;* the best solvent for it is boiling *oil of turpentine.* It gives by analysis 91·7 to 92·0 per cent. carbon, and 5·1 to 5·4 hydrogen, agreeing nearly with the formula above given—which requires 91·07 C, 5·11 H, and 2·92 O. (Bödeker, Ann. Ch. Pharm. lii. 100.) Dumas and Laurent regarded it as a hydrocarbon $C^{15}H^{10}$, but these results were calculated according to the old atomic weight of carbon.

Idrialin heated with strong *sulphuric acid* forms a solution of a fine blue colour, like that of sulphindigotic acid. The solution diluted with water forms with bases peculiar salts, among which the potassium-salt is distinguished by its beautiful crystalline character.—Idrialin boiled with strong *nitric acid* yields a red powder (Laurent's *nitrite of idrialase*) destitute of taste and odour, insoluble in water and ether, soluble in sulphuric acid, to which it imparts a mahogany colour. In potash it dissolves with brown colour. Heated in a closed tube, it decomposes with explosion and emission of light. According to Laurent's analysis, it contains 62·7 to 63·3 per cent. carbon, 3·2 to 3·0 hydrogen, and 10·5 nitrogen, approximating to the formula $C^{42}H^{23}(NO^2)^5O$. (65·2 C, 2·9 H, and 9·0 N).

IDRIALITE. The mineral from which idrialin is obtained. It is found in the quicksilver mine of Idria, mixed with cinnabar, and is sometimes called *inflammable cinnabar* (*Quecksilberbranderz*). It is massive and opaque, with greasy lustre, greyish or brownish-black colour, and blackish streak inclining to red. Specific gravity, 1·4 to 1·6. Hardness, 1 to 1·5.

IDRYL. Bödeker found in a product obtained by the dry distillation of the quicksilver ore of Idria in a close vessel, two peculiar hydrocarbons, one of which (*idryl*) formed mammellated groups, fusible at 86°, volatile without decomposition, very soluble in alcohol, ether, acetic acid, and oil of turpentine; while the other formed scales melting above 100°, volatilising before melting, and much more soluble than the former. Their composition agreed nearly with the formula, nC^3H^2 (94·7 C and 5·3 H).

IGASURIC ACID. Pelletier and Caventou (Ann. Ch. Phys. [2], x. 142). An acid contained, in very small quantity, combined with strychnine, in the bean of St. Ignatius; also in *nux vomica*, and in the root of *Strychnos colubrina.* It is prepared by washing the magnesia which has served for the preparation of strychnine, with cold water, till the colouring matter is removed, then boiling it with a large quantity of distilled water, which dissolves the igasurate of magnesium, precipitating it with acetate of lead, decomposing with sulphydric acid, and evaporating to a syrup. The acid is then deposited, after a while, in small hard granular crystals. It has a sour, styptic taste, and is very soluble in water and in alcohol. Corriol regards it as identical with lactic acid; but, according to Marsson (Ann. Ch. Pharm. lxxii. 296), this identity does not exist, for igasuric acid precipitates acetate of lead, which lactic acid does not.

The *igasurates* are for the most part soluble in water and in alcohol. The *ammonium-salt* is perfectly neutral, does not precipitate the salts of iron, mercury, or silver, but colours copper-salts green, and then forms a greenish-white precipitate sparingly soluble in water.

IGASURINE. An alkaloïd, discovered in 1853 by Desnoix (J. Pharm. [3], xxv. 202). It exists in *nux vomica*, and is found in the mother-liquors from which strychnine and brucine have been precipitated by lime at the boiling heat. These mother-liquors, if sufficiently concentrated, deposit the igasurine in crystals on the sides of the vessel. It may be purified by dissolving in water acidulated with hydrochloric acid, treating the solution with animal charcoal, precipitating by ammonia, and recrystallising.

Igasurine crystallises in colourless prisms, having a silky lustre. It is more soluble in *water* than strychnine or brucine, dissolving in 200 parts of cold and 100 parts of boiling water; it is sparingly soluble in *ether*, very soluble in *alcohol*. The alcoholic solution turns the plane of polarisation to the left: $[\alpha] = -62{\cdot}9^\circ$. It has not been analysed, but its atomic weight appears to be intermediate between those of strychnine and brucine.

Igasurine, when heated, melts and gives off water (about 10 per cent.); at a higher temperature, it is decomposed, with evolution of ammoniacal vapours. Strong *sulphuric acid* communicates to it a rose-colour, which passes to yellow, and then to yellowish-green. *Nitric acid* colours it deep red like brucine; on adding a few drops of stannous chloride, the colour changes to violet. *Chlorine*, passed into a very dilute solution of hydrochlorate of igasurine, produces first a rose, then a red, then a yellow colour, each bubble of gas being enveloped by a white pellicle, which is gradually deposited in the pulverulent form. If the stream of chlorine be discontinued, the precipitate redissolves on agitation, and the solution soon afterwards loses its red colour, retaining only a slight greenish tint. *Iodide of potassium*, added to a solution of igasurine, produces a crystalline precipitate after a considerable time; *iodurетted iodide of potassium* immediately forms a brown precipitate. Igasurine is not precipitated by chlorate of potassium, but its solutions yield a yellow precipitate with *dichloride of platinum*, white with *tannin*, and with *infusion of galls*.

Igasurine is intensely poisonous, being intermediate in power between strychnine and brucine.

Igasurine dissolves easily in dilute *acids*, and is precipitated from the solutions by *potash, soda, and ammonia*, the precipitate redissolving in excess of the alkali, especially in potash. It is also precipitated in needle-shaped crystals by *acid carbonate of sodium*, or *potassium*, in presence of tartaric acid.

The salts of igasurine are for the most part crystallisable. The *sulphate* forms colourless, silky crystals, soluble in about 4 pts. of boiling water, and 10 pts. of cold water. The *hydrochlorate* resembles the sulphate in form, but dissolves in 2 pts. of hot, and about 4 pts. of cold water. The *nitrate* forms colourless crystals, more soluble in water than either of the preceding salts.

According to Schützenberger (Compt. rend. xlvi. 1234; Ann. Ch. Pharm. cviii. 348), igasurine, prepared as above from the seeds of *Strychnos nux vomica*, yields by treatment with hot water, and fractional crystallisation, no fewer than nine distinct bases, all colourless, very bitter, and acting like strychnine. They crystallise in transparent needles, or in nacreous bulky geodes. They are reddened by nitric acid like brucine, which they also resemble in their chemical reactions, but they are more soluble in water and in alcohol. They all contain water of crystallisation (3 or 4 at.), which they give off at 100°. Schützenberger distinguishes them as *a*, *b*, *c*, &c. igasurine, and assigns to them the following formulæ:

Igasurine *a*. $C^{22}H^{26}N^2O^3.3H^2O$ very slightly soluble.
„ *b*. $C^{18}H^{24}N^2O^7.3H^2O$ slightly soluble.
„ *c*. $C^{18}H^{26}N^2O^4.3H^2O$ moderately soluble.
„ *d*. $C^{17}H^{22}N^2O^6.3H^2O$ „
„ *e*. $C^{18}H^{26}N^2O^4.3H^2O$ „
„ *f*. $C^{21}H^{26}N^2O^4.3$ or $4H^2O$ „
„ *g*. $C^{21}H^{28}N^2O^6.3H^2O$ very slightly soluble.
„ *h*. $C^{21}H^{26}N^2O^6.3H^2O$ moderately soluble.
„ *i*. $C^{20}H^{26}N^2O^7.3H^2O$ „

Igasurine *f* yields, by oxidation with nitrous acid, a base having the formula $C^{21}H^{26}N^2O^6$, which crystallises in colourless needles, containing 4 at. water, melting in their water of crystallisation at 100°, and coloured red by nitric acid.

In the absence of confirmatory evidences, these results must be considered rather doubtful.

IGLESIASITE. Syn. with HORN-LEAD. (See LEAD, CHLORIDE OF.)

IGLITE or **IGLOITE.** Syn. with ARRAGONITE (i. 358).

ILDEFONSITE. A columbite from Ildefonso, in Spain, having a submetallic vitreo-adamantine lustre. Specific gravity 7·416 (Dana, ii. 355).

ILICIC ACID. (Moldenhauer, Ann. Ch. Pharm. cii. 350).—An acid contained in the leaves of the holly (*Ilex aquifolium*). It is known only in combination with bases. To prepare the calcium-salt, an aqueous decoction of the leaves is precipitated with basic acetate of lead; the filtrate, freed from lead by sulphydric acid, is heated with hydrate of lead; the dissolved lead is again removed by sulphydric acid; and the filtrate is reduced to a syrup. The laminæ formed after some days are purified by pressing, dissolving in water, precipitating with alcohol, and recrystallising with the help of animal charcoal, whereby colourless ilicate of calcium is obtained.

Ilicate of calcium contains 12·86 per cent. calcium, and is readily soluble in water, but insoluble in alcohol. An aqueous solution does not precipitate salts of *manganese*, *zinc*, *iron*, *copper*, or *silver*, but produces a precipitate with *stannous chloride*, and with the *neutral* and *basic acetates of lead*. When the lead-salts are decomposed by sulphydric acid, a colourless syrup is formed, which still contains lime, and by neutralisation with carbonate of barium, yields amorphous ilicate of barium.

Holly-leaves gathered in January contain gum, or a similar substance, which interferes with the extraction of the acid.

ILICIN. The bitter principle of *Ilex aquifolium*. According to Déleschamps (Repert. Pharm. xli. 230), the decoction of the leaves is precipitated with basic acetate of lead; carbonate of potassium is added to make the liquid filter, and to precipitate any excess of the lead-salt; and the filtrate is acidified with dilute sulphuric acid, again filtered, saturated with carbonate of calcium, and evaporated to a syrup. Alcohol extracts from the syrup a light brown, very hygroscopic substance, which, in thin layers, dries up to small shining scales. Or, the aqueous extract is exhausted with alcohol, the alcoholic solution evaporated, and the dry residue exhausted with water at 40°. The filtrate is precipitated with basic acetate of lead, freed from excess of lead by sulphydric acid, evaporated, and treated with alcohol, which takes up the ilicin, and leaves it behind on evaporation. The aqueous solution of the alcoholic extract may also be treated, as above, with acetate of lead, dilute sulphuric acid, and carbonate of calcium in succession, the filtrate evaporated, and the ilicin extracted from the residue by alcohol. It is a bitter, amorphous, brown, very hygroscopic mass (still containing a little potash), converted by acids at a gentle heat into a black substance, with empyreumatic odour. It is soluble in water and alcohol, insoluble in ether.—Lebourdin (Ann. Ch. Pharm. lxvii. 254) agitates the decoction of the leaves with animal charcoal, then heats it therewith to boiling; leaves it to cool; removes the now colourless and tasteless liquid; washes the charcoal with cold water; boils it with alcohol; and leaves the filtrate to evaporate: it then leaves a colourless, very bitter syrup, and finally an amorphous, neutral jelly, easily soluble in water and in alcohol.—Moldenhauer's ilicin (Ann. Ch. Pharm. cii. 352) appears also to be different from this. Moldenhauer removes the alcohol from the alcoholic extract of the leaves by distillation, and the separated resin by filtration; precipitates with basic acetate of lead; washes the yellow precipitate, and decomposes it under water with hydrosulphuric acid. The sulphide of lead, after being well boiled with water, yields the ilicin to alcohol, as a very bitter, dark brown substance, resembling tannin, and slightly in water.—Bennemann (N. Br. Arch. xciii. 4) gives the name of ilicin to crystals which he obtains as follows: He precipitates the decoction with basic acetate of lead; decomposes the washed precipitate under water with sulphydric acid; filters the liquid from the sulphide of lead, and evaporates to dryness. By repeatedly exhausting the residue with alcohol, and leaving the solution to evaporate, needles were finally obtained, but not in sufficient quantity for further examination.

ILIXANTHIN. $C^{17}H^{22}O^{11}$. (Moldenhauer, Ann. Ch. Pharm. cii. 346.)—A substance occurring in the leaves of the holly (*Ilex aquifolium*). The leaves gathered in January contain scarcely any ilixanthin, while those gathered in August contain a large quantity. The leaves are exhausted with alcohol of 80 per cent.; the tincture thus obtained is freed from the greater part of the alcohol by distillation; and the residue is set aside to crystallise. The granules, which separate after some days, are dried, washed with ether to remove the green colouring matter of the leaves, dissolved in alcohol, and again separated by evaporation and addition of water; they are, lastly, recrystallised from hot water. A further quantity of ilixanthin may be obtained from the mother-liquor by reducing it to a syrup, dissolving in absolute alcohol, evaporating the alcoholic solution, dissolving the residue in water, and precipitating with basic acetate of lead. The washed precipitate is decomposed under hot water with sulphydric acid, and the filtrate is evaporated to a syrup, whereupon the ilixanthin crystallises out in straw-yellow microscopic needles, which melt at 198° to transparent red-yellow drops.

Ilixanthin boils and decomposes at 215°. It does not reduce an alkaline solution of *cupric oxide*, even on prolonged boiling. It is nearly insoluble in cold *water*, but dissolves easily in hot water, forming a yellow solution; also in *alcohol*, but is insoluble in *ether*. It dissolves in warm concentrated *hydrochloric acid*. The colour of the aqueous solution is changed to orange-yellow by *alkalis* and *alkaline carbonates*, but becomes colourless on addition of sulphuric acid. *Ferrous* and *cupric salts* do not affect ilixanthin; *ferric chloride* colours it green. Neutral or basic *acetate of lead* produces in the aqueous solution of ilixanthin a splendid yellow precipitate, soluble without colour in acetic acid.

Ilixanthin forms a yellow dye on cloth prepared with alumina or iron mordants.

ILMENITE. Titaniferous Iron. See TITANATES.

ILMENIUM. According to Hermann (J. pr. Chem. xxxviii. 91, 119; xl. 475; lxv. 52), Siberian yttrotantalite, or yttroilmenite, contains a peculiar metal which forms an acid, ilmenic acid, closely resembling niobic acid (see NIOBIUM), but, nevertheless, distinguished from it by its lower specific gravity, by the insolubility of its hydrate in hydrochloric acid, and by forming with sulphuric acid a compound which is decomposed by a large quantity of water, leaving a residue of hydrated ilmenic acid. According to H. Rose, however (Pogg. Ann. lxxi. 157), the supposed ilmenic acid is merely niobic acid, more or less impure. Rose also regards yttro-ilmenite as identical with uranotantalite or Samarskite (*q. v.*)

ILVAITE. See LIEVRITE.

IMABENZILE. $C^{14}H^{11}NO$. (Laurent, Rev. scient. x. 122; J. pr. Chem. xxvii. 312.)—Produced, together with benzilam and benzilimide, by the action of ammonia on benzile:

$$C^{14}H^{10}O^2 + NH^3 = C^{14}H^{11}NO + H^2O.$$

Benzile is dissolved in warm absolute alcohol; dry ammoniacal gas is passed through the still warm solution; and the liquid is left to cool, while the passage of the gas is continued. After 24 hours, the liquid, together with the sediment which has formed, is heated to the boiling point, and filtered at the same temperature. Imabenzile then remains on the filter, and may be purified by washing with ether.

Imabenzile is a white inodorous powder, which separates from its solution in boiling ether-alcohol, in microscopic right rhombic prisms with dihedral summits, whose faces rest on the obtuse lateral edges. It melts at 140°, remains soft and glutinous on cooling, and then solidifies without crystallising. It is quite insoluble in boiling alcohol and ether. It is partially decomposed during fusion. When subjected to dry distillation, it neither gives off gas nor leaves any carbonaceous residue. When gently heated with *nitric acid*, it gives off red vapours, and yields a yellow oil, which solidifies in the crystalline form on cooling, dissolves in alcohol, and crystallises therefrom in small needles united in tufts, but is insoluble in ammonia. It is not altered by boiling with hydrochloric acid. It dissolves in gently heated *sulphuric acid*, and the solution, mixed with water, deposits benzilam. It dissolves readily in boiling alcoholic potash; and water added to the solution throws down benzilimide, while nothing but potash remains dissolved.

IMASATIC ACID. Syn. with ISAMIC ACID.

IMASATIN. $C^{16}H^{11}N^3O^2$. (Laurent, Ann. Ch. Phys. [3] iii. 483.)—A compound produced by boiling a solution of isatin in ammonia. It is of a greyish-yellow colour, often inclining to brown or green, and crystallises sometimes in lamellated grains, sometimes in radiated spheres of a darker colour. It is insoluble in water and in ether, very sparingly soluble in boiling alcohol. It is decomposed by dry distillation, yielding a large quantity of charcoal and a sublimate of colourless needles. It is not attacked by boiling hydrochloric acid. Caustic potash dissolves it, and the solution, diluted with water and neutralised by an acid, yields a whitish, gelatinous precipitate.

Dichlorimasatin, $C^{16}H^9Cl^2N^3O^2$, is a powder of slightly reddish colour, produced by the action of ammonia on an alcoholic solution of chlorisatin.

Tetrabromimasatin, $C^{16}H^7Br^4N^3O^2$. Reddish-yellow scales produced by the action of ammonia on tetrabromisatin.

IMATRA STONES. Stony concretions found in a marly formation on the Schuttgebirg in Finland. They were regarded by Parrot (Petersb. Acad. Bull. 1839, vi. 183) as petrified molluscs, on the ground that they contained calcium and sulphur, neither of which elements were found by him in the formation in which they were imbedded. On the other hand, Virlet (Bull. Géol. ii. 219; iv. 22; Jahresber. 1847-8, p. 1298) regarded them merely as calcareo-aluminous concretions produced by molecular attraction. The concretions (*A*), and the formation (*B*) in which they are found, have been analysed by Ulex (Jahresber. 1861, p. 1086); the latter, also (B′) by Salvétat (*ibid.* 1298):

	SiO^2	Ca^2CO^3	Al^4O^3	Fe^4O^3	Mn^3O^4	H^2O	Alkali	TiO^2 and Mg^2O	
A.	70·3	. .	15·1	8·8	2·1	3·7	. .	. .	= 100·0
B.	31·8	51·1	8·2	6·5	2·4	. .	. .	. .	= 100·0
B′.	34·1	47·8	9·0	4·0	2·0	. .	0·5	traces	= 97·4

IMESATIN. $C^8H^6N^2O$. (Laurent, *loc. cit.*)—Obtained by passing dry ammonia gas into a boiling solution of isatin in absolute alcohol, in which a slight excess of pulverised isatin is suspended. It forms colourless right prisms, with rectangular base, inodorous, insoluble in water, moderately soluble in boiling alcohol, very sparingly in ether. Heated with a small quantity of alcohol and hydrochloric acid, it dissolves readily and decomposes, yielding isatin and sal-ammoniac. The same decomposition is produced by potash.

Chlorimesatin, $C^8H^5ClN^2O$, resembles imesatin, and is obtained in like manner from chlorisatin. It forms yellow hexagonal scales, sparingly soluble in boiling alcohol, nearly insoluble in ether. It is slowly decomposed by boiling water, with evolution of ammonia. When heated, it gives off ammonia, yields a sublimate of yellow needles, and leaves charcoal.

IMIDES. Monamides, in which 2 at. hydrogen are replaced by a diatomic radicle; *e.g. succinimide*, $N(CO)''H$; *pyro-tartrimide*, $N(C^5H^6O)''H$. (See AMIDES.)

IMPERATORIA OSTRUTHIUM. (*Masterwort.*)—The root of this plant (analysed by Keller) contains 0·2 per cent. of a resin called imperatorin or peucedanin; 16·0 fat and volatile oil; 5·6 extract soluble in water and alcohol; 8·8 gum and salts soluble in water; 9·2 starch and extract soluble in boiling water; 41·2 vegetable fibre, and 19·0 water (and loss). (Pelouze and Frémy, *Traité*, vi. 398.)

IMPERATORIN. See PEUCEDANIN.

INCINERATION. See ASH (i. 417).

INDELIBROMINE. $C^{16}H^8Br^4N^3O^4$.—A yellow substance, insoluble in water, produced by the action of bromine on isamic acid. (Laurent.)

INDIANITE. A variety of anorthite (i. 308) found in the Carnatic, differing somewhat from ordinary anorthite (from Vesuvius) in the composition of the protoxides which it contains. According to Laugier's analysis (Mem. du Mus. d. hist. nat. vii. 341), it contains 42·0 to 43·0 per cent. SiO^2, 34·0—34·5 Al^4O^3, 15·0—15·6 Ca^2O, 3·35—2·6 Na^2O, 3·20—1·0 Fe^4O^3, and 1·0 water.

INDIAN INK or **CHINA INK.** A black pigment, the best varieties of which are imported from China. It is composed of a very fine black, said by Prechot to be obtained from camphor, cemented together with gelatin.

INDIAN RED. A mineral from the Persian Gulf, used as a pigment. The hard coarse powder has a dark red colour, with a tinge of purple. Specific gravity 3·843. The following analyses, A, of the entire mineral, B, of the portion soluble in hydrochloric acid, are by How (Edinb. New Phil. J. new series, ii. 306; Jahresber. 1835, p. 925):

	SiO^2	Fe^4O^3	Al^4O^3	Ca^2O	Mg^2O	SO^3	CO^2	H^2O	
A.	30·17	56·59	3·79	2·65	1·43	2·28	1·73	1·62	= 100·26
B.	(. .	3·91	2·22	2·65	0·87	2·28	1·73	. .)	= 13·66

The principal portion (insoluble in hydrochloric acid) is a ferric silicate, $Fe^4O^3.3SiO^2$.

The name Indian red is also applied to another pigment of similar colour, consisting chiefly of sesquioxide of iron.

INDIAN YELLOW or **PURREE.** A yellow pigment consisting essentially of euxanthate of magnesium. (See EUXANTHIC ACID, ii. 609, and PURREE.)

INDICAN. $C^{26}H^{31}NO^{17}$ (Schunck, Phil. Mag. [4] x. 73; xv. 29, 117, 283; Jahresber. 1855, p. 660; 1858, p. 465.—Gm. xvi. 1.)—A colourless substance existing in woad, and most probably in other plants which yield indigo-blue. It likewise occurs in human urine, both healthy and diseased, and when present in considerable quantity, causes the urine, after spontaneous fermentation, or on addition of acids, to deposit, sometimes indigo-blue, sometimes indirubin. It may be detected by precipitating the urine with basic acetate of lead, collecting the precipitate which forms in the filtrate on addition of ammonia, and decomposing it with cold dilute acids, the filtrate then depositing, first, indigo-blue, then indirubin, and afterwards other products of the decomposition of indican. Indican is also found in the blood of man, and in the blood and urine of the ox. (Carter, Ed. Med. J., Aug. 1859.)

Preparation.—From woad-leaves, carefully dried and pulverised while warm.—1. The leaves are exhausted with cold alcohol in a percolating apparatus; the green tincture is precipitated with alcoholic sugar-of-lead and a little ammonia-water; and the pale green precipitate, after washing with cold alcohol, is decomposed under water by a stream of carbonic anhydride; it then loses its colour, and yields a yellow solution, which, when freed from dissolved lead by sulphydric acid, and evaporated over oil of vitriol, yields indican.—2. The tincture prepared with cold alcohol is concentrated, after addition of a little water, by passing a stream of air over it at the common temperature; the fat which separates is removed by filtration; the filtrate shaken up with recently precipitated cupric hydrate; the liquid again filtered; the filtrate freed from dissolved copper by sulphydric acid; and the liquid separated from the sulphide of copper is evaporated at the temperature of the air. From the residual brown syrup, cold alcohol dissolves out the indican, leaving undissolved a brown viscid mass which contains oxindicanin. By mixing the alcoholic solution with 2 vol. ether, further products of decomposition are precipitated, whilst the indican is obtained by evaporating the filtrate. When thus prepared it still retains a little fat.

Properties.—Indican forms a yellow or yellow-brown syrup, which cannot be dried without decomposing. It has a slightly bitter and repulsive taste, dissolves in *water*, with yellow colour, also in *alcohol* and *ether*. The alcoholic solution forms, with acetate of lead, a sulphur-yellow precipitate, which increases on addition of ammonia; the aqueous solution is precipitated by acetate of lead only after addition of ammonia.

Decompositions.—1. Indican decomposes even when gently warmed, and at a stronger heat swells up and emits vapours which condense to an oil, solidifying partially in the crystalline form.

2. The aqueous solution is decomposed by heat, and by spontaneous evaporation, yielding the following products:

a. Oxindicanin, $C^{20}H^{23}NO^{16}$. This compound separates on spontaneous evaporation, and may be purified by repeated solution in water and precipitation by alcohol. It is a brown viscid combustible gum, having a nauseous taste; by boiling with dilute sulphuric acid, it is resolved into indifuscin and indiglucin:

$$\underset{\text{Oxindicanin.}}{2C^{20}H^{23}NO^{16}} = \underset{\text{Indifuscin.}}{C^{24}H^{20}N^{2}O^{9}} + \underset{\text{Indiglucin.}}{2C^{6}H^{10}O^{6}} + 4CO^{2} + 3H^{2}O$$

b. Oxindicasin.—Produced when an aqueous solution of indican is evaporated by heat, the indican, according to Schunck, being first converted, with separation of indiglucin, into indicanin, the latter, with absorption of oxygen, into oxindicanin, and this last being resolved, with assumption of water, into oxindicasin and indiglucin:

$$\underset{\text{Oxindicanin.}}{2C^{20}H^{23}NO^{16}} + 3H^{2}O = \underset{\text{Oxindicasin.}}{C^{28}H^{32}N\ O^{23}} + \underset{\text{Indiglucin.}}{2C^{6}H^{10}O^{6}}$$

It is purified like the preceding, which it resembles. Its aqueous solution, precipitated with excess of neutral acetate of lead, yields a yellow lead-salt containing $C^{28}H^{32}N^{2}.4Pb^{2}O$.

c. Indicasin.—The liquid filtered from the lead-salt of oxindicasin, and containing excess of lead-acetate, yields, when treated with a large quantity of alcohol, a pale yellow precipitate = $C^{28}H^{40}N^{2}O^{23}.6Pb^{2}O$.

3. In contact with *soda-ley* or *baryta-water*, indican is resolved into indicanin and indiglucin:

$$\underset{\text{Indican.}}{C^{26}H^{31}NO^{17}} + H^{2}O = \underset{\text{Indicanin.}}{C^{20}H^{23}NO^{12}} + \underset{\text{Indiglucin.}}{C^{6}H^{10}O^{6}}$$

A solution of indican, left for several days in contact with soda-ley, yields, with acids, indirubin produced from the indicanin; after longer standing, indiretin is likewise obtained, and in some cases the latter is the only product.

4. Indican is decomposed by dilute *acids* in the cold, and more quickly when heated. The decomposition is induced by tartaric and oxalic acids, as well as by mineral acids, less easily by acetic acid. Aqueous indican mixed with dilute sulphuric acid, becomes turbid on standing, and deposits blue flocks, the formation of which ceases after 24 hours. The filtrate, after standing for some time, and still more when heated, deposits a brown powder, while leucine and indiglucin remain in solution, together with certain volatile products, viz. carbonic, formic, acetic, and perhaps propionic acid, which escape when the liquid is heated.

The substance insoluble in water is a mixture of six different bodies. On exhausting it, first with cold, then with warm dilute soda-ley, *indihumin*, *indifuscin*, and *indiretin* are dissolved; the residue yields to alcohol, *a*- or *β-indifulvin* and *indirubin*, together with residues of indifuscin, while *indigo-blue* remains in solution. Instead of indifuscin, *indifuscone* is sometimes obtained. Schunck gives the following formulæ:—

a. Formation of indigo-blue or its isomer, indirubin, and of indiglucin:

$$\underset{\text{Indican.}}{C^{26}H^{31}NO^{17}} + 2H^{2}O = \underset{\text{Indigo-blue.}}{C^{8}H^{5}NO} + \underset{\text{Indiglucin.}}{3C^{6}H^{10}O^{6}}$$

Part of the indigo-blue is said to split up into leucine, formic acid, and carbonic anhydride:

$$\underset{\text{Indigo-blue.}}{C^8H^5NO} + 5H^2O = \underset{\text{Leucine.}}{C^6H^{13}NO^2} + \underset{\text{Formic acid.}}{CH^2O^2} + CO^2$$

b. Formation of *α*-indifulvin, indiglucin, and formic acid:

$$2C^{26}H^{31}NO^{17} + 5H^2O = \underset{\alpha\ \text{Indifulvin.}}{C^{22}H^{20}N^2O^3} + \underset{\text{Indiglucin.}}{4C^6H^{10}O^6} + \underset{\text{Formic acid.}}{6CH^2O^2}$$

c. Formation of *β*-indifulvin, indiglucin, formic acid, and carbonic acid:

$$\underset{\text{Indican.}}{4C^{26}H^{31}NO^{17}} + 7H^2O = \underset{\beta\ \text{Indifulvin.}}{C^{44}H^{38}N^4O^3} + \underset{\text{Indiglucin.}}{8C^6H^{10}O^6} + \underset{\text{Formic acid.}}{10CH^2O^2} + 2CO^2$$

d. Formation of indihumin, indiglucin, propionic acid, and carbonic anhydride:

$$\underset{\text{Indican.}}{C^{26}H^{31}NO^{17}} + 2H^2O = \underset{\text{Indihumin.}}{C^{10}H^9NO^3} + \underset{\text{Indiglucin.}}{2C^6H^{10}O^6} + \underset{\text{Propionic acid.}}{C^3H^6O^2} + CO^2$$

e. Formation of indifuscone, indiglucin, acetic acid, and carbonic anhydride

$$\underset{\text{Indican.}}{2C^{26}H^{31}NO^{17}} + 3H^2O = \underset{\text{Indifuscone.}}{C^{22}H^{20}N^2O^5} + \underset{\text{Indiglucin.}}{4C^6H^{10}O^6} + \underset{\text{Acetic acid.}}{2C^2H^4O^2} + 2CO^2$$

f. Formation of indiretin, indiglucin, carbonic anhydride, and water:

$$\underset{\text{Indican.}}{C^{26}H^{31}NO^{17}} = \underset{\text{Indiretin.}}{C^{18}H^{17}NO^5} + \underset{\text{Indiglucin.}}{C^6H^{10}O^6} + 2CO^2 + 2H^2O$$

INDICANIN. $C^{20}H^{23}NO^{12}$. (Schunck, Phil. Mag. [4] xv. 183.)—This compound is produced, together with indiglucin, by the action of aqueous alkalis or baryta-water on indican:

$$C^{26}H^{31}NO^{17} + H^2O = C^{20}H^{23}NO^{12} + C^6H^{10}O^6.$$

Indicanin is left in contact with baryta-water; the liquid is precipitated with dilute sulphuric acid; and the filtrate is freed from excess of sulphuric acid by carbonate of lead, from lead by sulphydric acid, and evaporated in a stream of air at mean temperature. The residue is dissolved in alcohol; the solution is mixed with twice its volume of ether, which precipitates indiglucin; and the filtrate is left to evaporate.

Indicanin is a yellow or brown bitter syrup, soluble in *water*, *alcohol*, and *ether*. When heated on platinum-foil, it swells up strongly and leaves charcoal. By dry distillation it yields a brown oil in which white needles form. When boiled with *acids*, it yields indiglucin and indirubin, and if impure, likewise indiretin and indifuscin. Formation of indirubin:

$$C^{20}H^{23}NO^{12} + H^2O = C^8H^5NO + 2C^6H^{10}O^6.$$

When boiled with *soda-ley*, it gives off ammonia.

Aqueous indicanin forms a slight precipitate with neutral acetate of *lead;* from alcoholic indicanin an alcoholic solution of neutral acetate of lead throws down a copious sulphur-yellow precipitate, soluble in excess of the lead-acetate, precipitable by ammonia, and containing $C^{20}H^{23}NO^{12}.3Pb^2O$.

INDIFULVIN. (Schunck, *loc. cit.*)—This name is applied to two compounds, distinguished as *α* indifulvin, $C^{22}H^{20}N^2O^3$, and *β* indifulvin, $C^{44}H^{38}N^4O^3$, which are obtained, together with indifuscin, indiglucin, indigo-blue, indihumin, indiretin, and indirubin, by treating indican with dilute acids.

Preparation.—Indican is heated with dilute sulphuric acid; the flocks which separate are collected (the solution which runs off being preserved for the preparation of indiglucin), washed with cold water, and treated, first with cold, then with warm dilute soda-ley, which dissolves one portion, and leaves another containing *α*- and *β*-indifulvin, indirubin, and indigo-blue. The alkaline solution is precipitated with hydrochloric acid, and the precipitate is collected, washed, and treated with boiling ammonia, which dissolves indifuscin and indiretin, and leaves indihumin. The ammoniacal solution, neutralised with acetic acid, yields a precipitate of indifuscin, and an additional quantity of this product is precipitated from the filtrate by alcoholic sugar-of-lead. The indiretin which still remains in solution is separated by ammonia, in combination with lead-oxide and contaminated with indifuscin; it is separated from the lead-oxide by treating the precipitate with acetic and then with hot hydrochloric acid, and purified by repeated solution in alcohol, which leaves the indifuscin undissolved.

The mixture of *α*- and *β*-indifulvin, indirubin, and indigo-blue, insoluble in dilute soda-ley, gives up to boiling alcohol everything excepting the indigo-blue. The purple-brown alcoholic solution, mixed with ammonia and alcoholic sugar-of-lead, deposits residues of substances soluble in soda-ley; and on separating these, then adding excess of acetic acid, distilling off the alcohol, and diluting largely with water, purple-brown flocks are obtained, from which, when purified with dilute soda-ley, a small quantity of cold alcohol extracts indifulvin. On boiling the residue with an alkaline solution of protochloride of tin, filtering hot, and exposing the filtrate to the air, a purple-red deposit is formed, consisting of indirubin. This is washed with water and dissolved in alcohol. The portion insoluble in the alkaline solution is a mixture of indirubin and indifulvin.

Indifulvin is obtained of various composition, α or β, according to circumstances not well understood. It is a brittle, friable, reddish-yellow resin, which, when heated, melts, burns with flame, and leaves charcoal. Heated in a glass tube, it gives off a strong-smelling vapour, condensing to a brown oil, which solidifies in the crystalline form. Dissolves in strong *sulphuric acid*, with green-brown colour, and chars when heated. By ordinary *nitric acid*, it is scarcely attacked, even at the boiling heat; but it dissolves in fuming nitric acid, and is precipitated by water in orange-yellow flocks. By heating and evaporating the liquid, a yellow resin is obtained, together with crystals soluble in water, and different from oxalic acid. It is slowly decomposed by *chromic acid*. It does not dissolve in aqueous *alkalis*, even at the boiling heat, or on addition of grape-sugar, or dichloride of tin.

INDIFUSCIN, $C^{24}H^{20}N^2O^3$, and **INDIFUSCONE**, $C^{22}H^{20}N^2O^4$?—These compounds are produced in greatest quantity by the action of dilute sulphuric acid on indican which has been previously exposed to the air. A brown powder is then formed, containing from 59·4 to 67·5 per cent. C, 5·78 to 7·12 N, and 29·12 to 20·23 O, so that it appears to agree, sometimes with one, sometimes with the other of the formulæ just given. When heated, it emits vapours, with an odour of burning turf, and yields an oily distillate. It burns without fusion; colours *chromic acid* green; with boiling *nitric acid*, it yields oxalic and picric acids; dissolves in strong sulphuric acid, with brown colour, giving off sulphurous anhydride when heated. It is insoluble in boiling water; dissolves easily in alcoholic *ammonia*, whence it is precipitated in brown flocks by acids; also in aqueous *alkalis* and *alkaline carbonates*, and is precipitated therefrom by *metallic salts;* sparingly soluble in boiling *alcohol*.

INDIGLUCIN. $C^6H^{10}O^6$. (Schunck, Phil. Mag. [4] x. 73; xv. 183; Jahresber. 1856, 659; 1858, 465; Gm. xv. 302.)—Produced, together with the products above mentioned, by heating indican, indicanin, oxindicanin, or oxindicasin, with water, acids, or alkalis (pp. 247, 248).

Preparation.—Tincture of woad-leaves, prepared with cold alcohol, is evaporated in a current of air; the residue is mixed with cold, very dilute sulphuric acid, and the fat which falls to the bottom is immediately separated by filtration. The filtrate serves instead of the acidulated aqueous solution of indican. The decomposition, which begins in the cold, is kept up by gentle heating, whereupon the solution becomes turbid, and a mixture of six insoluble substances separates (p. 247); the liquid is then filtered, the residue washed with cold water, and decomposed in the manner described under indican. The filtrate, freed from sulphuric acid by carbonate of lead, and from lead by sulphuric acid, evaporated to a syrup in a stream of air, dissolved in alcohol, and mixed with a large quantity of ether, deposits leucine in crystals, and indiglucin as a syrup. The latter, after the removal of the crystals, is dissolved in water; the solution is mixed with acetate of lead; the scanty precipitate is removed; and the yellow lead-compound of indiglucin is precipitated from the filtrate by aqueous ammonia. The lead-salt decomposed by sulphydric acid under water, and treated with animal charcoal till a sample gives a white precipitate with ammoniacal sugar-of-lead, yields a solution from which, by evaporation, solution of the residue in alcohol, and addition of ether, the indiglucin is precipitated in the form of a syrup.—2. In the preparation of indicanin from indican, by mixing the latter with baryta-water and leaving it at rest, then removing the baryta, evaporating the filtrate in a current of air, dissolving the residue in alcohol, and precipitating by ether, indiglucin is separated as a syrup. This syrup is dissolved in alcohol, mixed with excess of alcoholic sugar-of-lead, the brown precipitate removed, and the solution precipitated with ammonia. The lead-compound of indiglucin is purified and decomposed as in method 1.

Indiglucin is a colourless or light yellow syrup having a slightly sweet taste, soluble in *water* and in *alcohol*; but precipitated from the alcoholic solution by *ether*.

It swells up when heated, and gives off an odour of caramel. With boiling *nitric acid*, it forms oxalic acid. With strong *sulphuric acid*, it becomes carbonised. When boiled with *soda-ley*, it turns yellow, and separates brown flocks. From an *alkaline cupric solution* it reduces cuprous oxide; from an aqueous and still more from an *ammoniacal* solution of *nitrate of silver*, it reduces metallic silver; similarly with *trichloride of gold*. It is not fermentable, but turns acid by prolonged contact with *yeast*.

Aqueous indiglucin dissolves *hydrate of calcium*, and the solution on boiling deposits copious yellow flakes, which dissolve on cooling, and are precipitated by alcohol. From a mixture of indiglucin with *baryta-water* alcohol throws down yellow flakes.—Aqueous indiglucin is precipitated by neutral or basic acetate of *lead*, only after addition of ammonia; the precipitate has the composition $2C^6H^9PbO^6.3Pb^2O$.

INDIGO-BLUE. C^8H^5NO or $C^{16}H^5NO^2$.—*Blue Indigo. Indigotin. Oxidised Indigo* (Gm. xiii. 35; Gerh. iii. 514).—This important colouring matter was known in India and in Egypt before the Christian era, and is mentioned by Dioscorides and Pliny under the names *ἰνδικόν* and *indicum*. Egyptian mummies have been found wrapped in blue cloths, the colour of which exhibited all the characters of indigo. The Romans used it only as a pigment, not being acquainted with the method of dissolving it. Its introduction into Europe as a dye is generally attributed to the Jews, who during the middle ages practised the art of dying with indigo in the Levant. It was first imported in large quantities into the European markets from India in the seventeenth century by the Dutch.

Indigo is chiefly obtained from various species of *Indigofera*, namely, *I. tinctoria*, *I. Anil*, *I. disperma* and *I. pseudotinctoria*, cultivated especially in the East and West Indies; also from *Nerium tinctorium* and *Calanthe veratrifolia*, natives of Hindostan; *Asclepias tinctoria* and *Marsdenia tinctoria* of Sumatra, *Polygonum tinctorium*, *Isatis indigotica*, *Justicia tinctoria* and *Bletia Tankervilliæ* of China, and *Amorpha fruticosa* of Carolina. The only European plant which yields true indigo-blue is woad (*Isatis tinctoria*), which was extensively used for blue-dyeing before the introduction of indigo; but it is much less rich in indigo than the tropical plants above mentioned, and is now used only as an addition to the indigo-vat (p. 252). The following European plants also yield blue colouring matters more or less resembling indigo, but apparently not identical with it: *Astragalus glycyphyllus*, *Centaurea Cyanus*, *Chelidonium majus*, *Cicer arietinum*, *Colutea arborescens*, *Coronilla Emerus*, *Galega officinalis*, *Hedysarum Onobrychis*, *Inula Helenium*, *Iris germanica*, *Lotus corniculatos*, *Medicago sativa*, *Mercurialis perennis*, *Polygonum aviculare*, *Polygonum Fagopyrum*, *Rhinanthus Crista-galli*, *Sambucus nigra*, *Sambucus Ebulus*, *Scabiosa succisa and Vaccinium Myrtillus.*

Indigo-blue is sometimes deposited from human urine both healthy and diseased, being produced by spontaneous fermentation from indican (p. 246). It has also been occasionally observed to form in the milk of cows, especially such as have been fed exclusively on sainfoin.

With regard to the state in which indigo exists in the plants from which it is obtained, and the nature of the process by which it is converted into indigo-blue. various opinions have been entertained. Roxburgh (*Transactions of the Society of Arts*, vol. xxviii.) supposed that indigo plants contain only the base of the colouring matter, which of itself is green; that it is kept in solution by the carbonic acid evolved in the preparation of indigo, set free by the addition of alkalis, and absorbs from the air a substance which converts it into indigo-blue. Giobert (*Traité sur le pastel*, Paris 1813) supposed that indigo-plants contain colourless **indigogen**, which is soluble in water and contains more carbon than indigo-blue, into which it is converted, with formation of carbonic acid, by absorbing oxygen from the air. This oxidation is promoted by heat or by the presence of alkalis, especially by lime; it is arrested by acids, even by carbonic acid. (Giobert.)

According to Chevreul (Ann. Chim. lxvi. 8; lxviii. 284), woad and other indigo-plants contain indigo-white, C^8H^6NO, which contains 1 at. H more than indigo-blue. and being held in solution by the sap, is converted into indigo-blue by oxidation, on exposure to the air:

$$2C^8H^6NO + O = 2C^8H^5NO + H^2O.$$

This explanation, being the simplest, was very generally adopted, until Schunck (Phil. Mag. [4] xv. 29) pointed out that white indigo cannot exist in any plant, since it requires free alkali for its solution, whereas the sap of plants is always acid, and moreover contains free oxygen. Schunck has further shown that woad contains indican, (p. 246), which is readily soluble in water, and when boiled with acids splits up into indigo-blue and indiglucin, without the intervention of oxygen:

$$\underset{\text{Indican.}}{C^{26}H^{31}NO^{17}} + 2H^2O = \underset{\text{Indigo-blue.}}{C^8H^5NO} + \underset{\text{Indiglucin.}}{3C^6H^{10}O^6}.$$

The same substance probably exists in other indigoferæ, and in other plants from which indigo is obtained, and during the steeping process, presently to be described, is resolved, in consequence of the fermentation which takes place, into indigo-blue and indiglucin.

Preparation of Commercial Indigo.—1. *From fresh leaves.*—In Bengal, the plants, which are cut close to the ground whilst the blossom is unfolding, are placed in a brick cistern (*steeping vat, Gährungsküpe, trempoire, pourriture*), which is filled several inches deep with cold water, and allowed to ferment. At 30° C. (86 F.) the fermentation is finished in from 12 to 15 hours; at lower temperatures it requires a longer time. The gas evolved is a mixture of carbonic anhydride and atmospheric air from which the oxygen has been absorbed. When the liquid no longer rises, it is drawn off into the *beating vat* (*Schlagekūpe, batterie*) which stands lower, where it is kept stirring for an hour and a half or two hours, whereupon carbonic anhydride is evolved and the indigo at first separates in large flakes. When, after being repeatedly stirred, it forms grains like fine sand, and the solution is clear, the indigo is allowed to settle. After two or three hours, the liquid is drawn off from the deposit. If the fermentation is properly conducted, the indigo settles readily down, the liquid is of a malaga-brown colour, and forms a thick foam which rapidly disappears. The deposit is boiled for three or four hours in a copper vessel and then thrown upon a linen filter; it is afterwards pressed, cut into squares, and dried by heat. 1000 pts. of the solution of the leaves yield from 0·5 to 0·7 pts. of indigo; more is precipitated on the addition of potash-ley or lime-water, but it is not so pure.

Respecting the manufacture of indigo in the Caucasus, see *Dingl. pol. J.* 126, 304.

2. *From dry leaves.*—In the southern parts of India, the leaves of the indigo plant are dried, and packed up for a month, more or less, at the expiration of which time they assume a light lead colour; by additional keeping the lead-colour gradually darkens till it becomes black. Experience has proved that the leaves will not give out any colouring matter to cold water till the first change has commenced, when the maximum quantity of indigo seems to be developed; and that from this period it diminishes. If from fear of rain the plant be cut too soon, the leaves should be kept proportionally longer; but if, from want of sufficient sunshine, the cutting be deferred till after the plant is fully ripe, the leaves will not require to be kept so long.

These leaves, after due keeping, are transferred to the steeping-vat, where they are infused in water, in the proportion of about one volume of leaves to six of water, and allowed to digest for two hours, with occasional stirring. The water is then run off through strainers into the beating-vat, where it is agitated by the paddles of ten or twelve natives for about two hours, during which time the fine green liquor gradually darkens to a blackish hue. Lime-water is now thrown into the vat, and well mixed with the liquor. The supernatant Madeira-coloured liquid is run off after repose, and the subsided blue indigo is drained on cloth. Next morning it is mixed with water in a copper and boiled; after which the whole is thrown on strainers, and the indigo collected is dried and formed into cakes. (Weston, *Journal of Science*, xxvii. 296.)

Indigo is obtained in the same way in the south of France from a hot extract of *Nerium tinctorium* and *Polygonum tinctorium* (J. Pharm. xxvi. 276; J. pr. Chem. xvi. 180). Indigo was formerly prepared from woad in a similar manner, by employing tepid water and precipitating with lime-water; a deeper colour was imparted to the product by extracting the carbonate of calcium with hydrochloric acid. The preparation of indigo from *Polygonum tinctorium* is rendered difficult by a resin which the plant contains. This resin is separated by mixing the bruised leaves with one-tenth of their weight of protosulphate of iron, and adding a sufficient quantity of water, together with an excess of carbonate of potassium; the whole is then thrown upon a filter, and the solution mixed with sufficient nitric acid to render it slightly acid. On neutralising with carbonate of potassium, it becomes blue and deposits all the indigo-blue within 24 hours; the indigo has then the same properties as that obtained from *Indigofera*. (Gaudry, N. J. Pharm. v. 133.)

Purification.—Commercial indigo contains from 50 to 60 per cent. of pure indigo-blue, the remainder consisting of indigo-gluten, indigo-red, indigo-brown, and a number of brown resinous products, &c., formed either by decomposition of the indigo-blue produced in the first instance, or directly from the indican itself (p. 246). Certain substances are also occasionally added to indigo for the purpose of adulteration.

Indigo may be purified from most of these foreign matters by treating it successively with dilute sulphuric or hydrochloric acid, with boiling water, and with alcohol. This treatment however does not yield a chemically pure product, and it is better to resort to the process of the vat, which consists in converting the indigo-blue into indigo-white by the action of reducing agents, and subsequently reoxidising it. This process is also one of great industrial importance, being that which is used by dyers for rendering indigo soluble and fixing it upon tissues.

a. Cold Vats.—1. *Copperas* or *common blue vat.* (*Cuve à la coupĕrose, Vitriolküpe.*) In this, which is the kind of cold vat generally used for dyeing cotton, hemp, and flax, the indigo-blue is reduced by the action of protosulphate of iron. 1 pt. of finely ground indigo is mixed with hot water, in which 4 pts. of quick-lime are slaked; to this is added a solution of 3 pts. of sulphate of iron free from copper, the whole being stirred. (If the sulphate of iron is yellowish, one-third more is taken.) Water is added, to the amount of 100 or 200 times the weight of the sulphate of iron, according as the dye is required dark or light, and the whole, after being stirred, is left at rest. The proportions quoted are those most commonly used in dyeing; when the indigo is particularly pure, more lime and sulphate of iron must be taken. An excess of lime yields a *sharp* vat (*scharfe Küpe*), from which the threads of the material do not readily take up the dye; too little lime yields a *soft* vat (*leise Küpe*), which does not dye so well. On the addition of carbonate of potassium, a compound of indigo-white with potash is formed. A sediment is formed and a yellow solution, which becomes covered with a copper-coloured film (flower); the solution is drawn off from the sediment, and deposits tolerably pure indigo-blue on exposure to the air.—Thomson digests commercial indigo with lime, sulphate of iron, and water, and exposes to the air the decanted solution of the compound of indigo-white with lime; he then removes the carbonate of calcium from the blue precipitate with hydrochloric acid, and the indigo-red with water, afterwards washes with water and dries.—Berzelius mixes 3 pts. of indigo (purified according to 1) with 6 pts. of quick-lime freshly slaked, 4 pts. of sulphate of iron, and 450 pts. of boiling water; he then closes the vessel and shakes repeatedly; allows the whole to subside, and removes the yellow solution by means of a siphon; again adds hot water, and draws it off after repeated shaking; and mixes the whole of the solution with hydrochloric acid; this is exposed to the air and shaken till the indigo is completely oxidised; it is then thrown on a filter and washed with water. —Erdmann mixes together 1 pt. indigo, 2 pts. sulphate of iron, 3 pts. lime, and 60 pts. water; draws off the clear solution; mixes it, stirring repeatedly, with dilute hydrochloric acid; and washes the precipitate in contact with the air. The residue yields fresh quantities of indigo-blue when again stirred up with hot water, and with lime if necessary. The indigo-blue thus obtained contains a little gypsum, at most 0·75 per cent., and indigo-red, which it is difficult to remove by boiling with alcohol; it is better to reduce the indigo again in the cold vat and precipitate it with hydrochloric acid.—According to Dumas, a little sulphide of calcium is formed in the vat, and hence sulphur is mixed with the indigo when it is precipitated by hydrochloric acid; this he removes with sulphide of carbon.

2. In the so-called *orpiment-vat*, a solution of the compound of indigo-white with potash is formed in a mixture of indigo-blue with trisulphide of arsenic, potash, and water, by the oxidation of the resulting sulpharsenite of potassium; the solution deposits indigo-blue when exposed to the air. This kind of vat is chiefly used for calico-printing, not for dyeing properly so-called.

3. In the *tin-vat*, commonly used for calico-printing, the indigo is reduced by a solution of stannous oxide in caustic potash or soda. The bath is usually mixed with an acid solution of tin, so as to neutralise the alkali and precipitate the indigo-white; the precipitate is then used for printing.

b. Warm vats.—1. *Woad-vat.* (*Pastel-vat.*) On mixing from 2 to 6 pts. of finely powdered indigo with from 30 to 50 pts. woad, 2 pts. madder, 2 pts. bran, 1 to 8 pts. potash, and ½ pt. lime, and warming with 1000 pts. water (6000 to 7000 litres) at 80° C. (176° F.), a fermentation is set up in which water is decomposed and the nascent hydrogen forms indigo-white, which combines with the ammonia simultaneously formed. The brownish-yellow liquid first becomes green on exposure to the air, and then deposits indigo-blue; it may be used for dyeing for three to six months, provided it be kept warm, and madder, bran, indigo or potash added from time to time as required. Beetroot-molasses and malt may be advantageously used instead of madder. The use of madder, bran, &c. in this process appears to depend upon the gummy and amylaceous substances and the pectic acid which they contain. These substances are probably transformed, first into lactic, then into butyric acid, in which transformation hydrogen is evolved, which reduces the indigo-blue to indigo-white. The woad at the same time undergoes putrefaction, and gives off ammonia, which keeps the indigo-white in solution. The lime seems to act chiefly by neutralising the excess of acid produced by the decomposition of the amylaceous and gummy matters.

2. In the *potash* or *Indian vat*, in which woad and lime are not used, 3 pts. of indigo are added to a mixture of 2 pts. madder, 2 pts. wheat-bran, 6 pts. potashes, and 1000 pts. water at 60° C. (140° F.); after 36 hours, 3 pts. potashes, and after 12 hours more the same quantity of potashes, are likewise added. This vat is easier to manage than the woad vat.

3. The *urine-vat* is employed only in small dye-houses and in certain localities, as at Verviers, for the dyeing of wool. The putrefying urine furnishes at once the reducing agents to convert the blue into white indigo, and the ammonia necessary to dissolve the latter. [For further details respecting the manufacture of indigo and its use in dyeing, see *Ure's Dictionary of Arts, &c.* ii. 498.]

To obtain indigo-blue in the crystalline state, 4 oz. of raw indigo and 4 oz. of grape-sugar are introduced into a flask capable of containing 12 lbs. water, to which 6 oz. of the strongest soda-ley are added. The whole is well shaken, and the flask completely filled with hot alcohol; it is then tightly corked and allowed to stand for several hours, until the solution is sufficiently clear to permit its being siphoned off into a larger flask. The flask is allowed to stand loosely covered; the solution, at first of a beautiful yellowish-red colour, now gradually turns blue, whilst indigo separates out. The solution is filtered and the indigo is washed, first with alcohol and then with water, till the filtrate is colourless. In this manner, 2 oz. (50 per cent.) of pure indigo-blue is obtained. If the brown alcoholic solution is poured back hot into the first flask, it yields 3 per cent. more indigo; but it is then nearly exhausted (**Fritzsche, Marchand**).--Indigo also forms a vat immediately with grape-sugar, caustic soda, and hot water; the decanted solution, when exposed to the air, deposits indigo-blue containing a quantity of indigo-red, which may be extracted by an alcoholic solution of soda. (**Fritzsche.**)

Purification of indigo by sublimation.—When powdered commercial indigo is heated on a watch-glass, a silver dish, or a spoon, a network of crystals is formed, which may be removed with a pair of forceps, and the crystals carefully separated from adhering particles of carbon, under a magnifying glass (**Le Royer** and **Dumas**; **Dumas**).—**Crum** heats indigo between two platinum crucible lids, which are separated from one another by a distance not greater than ⅜ inch, till the hissing sound ceases.—**Berzelius** sublimes indigo in an exhausted retort, of the size of a chicken's egg, cuts off the upper part of the retort when the crystals have sublimed, and separates the lower crystals from the adhering particles of carbon. The crystals are freed by ether from traces of oil and resin.—**Taylor** stirs up an intimate mixture of 2 pts. finely powdered indigo and 1 pt. gypsum with water into a thin paste, which he spreads upon sheet iron in layers 2 inches broad and ¼ inch deep. These are dried by exposure to the air, then heated at one end with a spirit-lamp till red vapours are evolved, and so the operation is continued. If the mass catches fire, it is extinguished by a drop or two of water. The velvety indigo can easily be separated, and may be purified by alcohol and ether. (Med. Gaz. 1843, 130.)

Preparation of Indigo-blue from Indican.—The aqueous solution of indican from woad-leaves, which must not be too dilute, is boiled with sulphuric acid or hydrochloric acid; and the abundant purple-blue precipitate is filtered off and washed, first with water and then with boiling alcohol, till the filtrate is of a pure blue colour: the residue consists of pure indigo-blue. Nitric, oxalic, tartaric, and acetic acids are also capable of converting indican into indigo-blue: acetic acid, however, acts less powerfully than the rest. (**Schunck.**)

Properties.—Indigo-blue sublimes in right rhombic prisms (**Miller**); in six-sided prisms derived from a rhombic prism of 32° and 148°, and having their bases replaced by two faces which seem to form an obtuse angle with one another (**Laurent**). Its lustre is semi-metallic, and by reflected light, dark-red inclining to copper-red (according to Crum, it is red when viewed obliquely under the microscope; and of a brilliant blue when viewed perpendicularly). When prepared in the wet way, it is dark blue, and acquires by pressure a dark copper colour and almost metallic lustre. It is inodorous and tasteless, and does not react upon vegetable colours.—In open vessels, it volatilises at about 288° in dark purple-red vapours; in closed vessels, it decomposes partially when heated (**Crum**). It volatilises without decomposition only in a current of air or in vacuo; the powder dropped on a piece of heated platinum foil, volatilises in purple vapours without leaving a residue, each particle being supported by the vapour without coming in contact with the foil (**Dumas**). It is quite insoluble in *water*, dilute *acids*, and *alkalis*, *ether*, and *volatile oils;* also in *alcohol* and *fixed oils* at common temperatures; but hot alcohol, and fixed oils heated above 100°, dissolve small quantities, and deposit it again on cooling. Sublimed indigo dissolves pretty readily in hot *phenic acid*, forming a blue liquid when mixed with a little alcohol, but precipitated by a larger quantity. Sublimed indigo also dissolves to a small extent in hot *oil of turpentine.*

Indigo-blue is isomeric with cyanide of benzoyl.

Decompositions.—1. Indigo-blue melts and boils when heated in contact with the *air;* at higher temperatures it burns with a bright and very smoky flame, leaving a residue of difficultly combustible charcoal (**Berzelius**). By exposure to air containing *ozone* it is quickly converted into isatin. (**Erdmann**, J. pr. Chem. lxxi. 209.)

2. By dry distillation, it yields a very little undecomposed sublimate, together with carbonate and cyanide of ammonium, phenylamime, empyreumatic oil, and a large residue of shining charcoal (**Crum**). On heating indigo-blue in vacuo, a brown oil is formed, together with a large proportion of sublimed indigo, but no permament gas or aqueous liquid; by rapid heating, more sublimate is obtained, and a fused shining charcoal; on heating more gradually, less sublimate is formed, together with a dull earthy charcoal. (**Berzelius.**)

3. Dry *chlorine* does not act upon indigo-blue between 0° and 100°. If indigo-blue is stirred up with water into a thin paste, and chlorine passed through while the whole is kept cool, the mass becomes first greyish-green and then yellow. Neither carbonic anhydride nor any other gas is evolved. An orange-coloured deposit is

formed, and a yellowish-red solution; on distilling, trichlorophenic acid and trichlorophenylamine sublime, and a liquid distils over which smells of anisic acid, and contains hydrochloric and trichlorophenic acids. The residue in the retort dissolves in boiling water, leaving a brown resin, which is formed in small quantity only. If the mass is cooled as much as possible during the action of the chlorine, and the passage of the chlorine is interrupted before all the indigo-blue is destroyed, the boiling aqueous solution deposits, on cooling, a yellowish-red crystalline powder, which yields chlorisatin and dichlorisatin when recrystallised from alcohol. (Erdmann.)

4. *Bromine* acts upon indigo in the same manner as chlorine. On treating moist indigo with bromine, a yellow mass is formed, which yields, by distillation, tribromophenic acid and tribromophenylamine; the residue contains a little bromisatin, a large proportion of dibromisatin, and a little resinous matter. (Erdmann.)

5. *Iodine* decomposes indigo only when heated. (Berzelius.)

6. Indigo is decomposed by heating it with *chlorate of potassium* and *hydrochloric acid*. Only traces of chloranil are formed. (Hofmann.)

7. When boiled with dilute *nitric acid*, it gives off a large quantity of gas, and forms isatin and a brown resin; with a stronger acid, it forms principally nitrosalicylic acid, and with an excess of nitric acid of specific gravity 1·43, it yields picric acid; at the same time carbonic anhydride, prussic acid, oxalic acid, and the so-called artificial indigo-resin are formed. 5 pts. of fuming nitric acid becomes so violently heated with 1 pt. powdered commercial indigo that the mass takes fire.

8. Concentrated *chromic acid* destroys indigo-blue immediately, especially when heat is applied, with violent evolution of carbonic anhydride and precipitation of sesquioxide of chromium. Dilute chromic acid forms a clear yellow-brown solution with indigo; if this is heated to near the boiling point and filtered, isatin crystallises out on cooling (Erdmann). Chlorochromic acid does not act upon indigo-blue. (Thomson.)

9. On boiling indigo-blue with *peroxide of lead*, a pale yellow solution is formed, which becomes turbid on cooling, and leaves a yellow powder when evaporated to dryness. This substance being suspended in water and decomposed with sulphydric acid, yields a brownish-yellow filtrate, which on evaporation leaves a residue consisting of a small quantity of brown resin and a few crystals. The sulphide of lead contains a brown resin, melting at 100°, which may be extracted by boiling alcohol, and precipitated by water; boiling water extracts from it a substance which, on evaporation, deposits crystals mixed with resin. (Erdmann.)

10. *Manganic sulphate, manganate of potassium*, and *permanganate of potassium* decolorise indigo (Lefort, Rev. scient. 16, 358). On heating indigo-blue for a considerable time with aqueous *osmic acid*, oxalic acid is formed. (Buttlerow, J. pr. Chem. lvi. 278.)

11. When the vapour of *sulphuric anhydride* is passed over roughly pulverised commercial indigo, the latter swells up, becomes heated, and a beautiful purple-red liquid is formed, which is transparent in thin layers, and solidifies into a crimson mass. In contact with the air, it evolves sulphurous anhydride (probably on account of the impurities of the indigo), and dissolves in common sulphuric acid with a violet colour; on dissolving it in water, charcoal separates out and a dark blue solution is formed (Döbereiner; Bucholtz; Bussy). Indigo dissolves, with evolution of heat, in excess of fuming or of common *sulphuric acid* (no gas is evolved if the indigo is pure) with formation of sulphindigotic acid; if an excess of sulphuric acid is not added, more or less sulphophœnicic acid is formed. According to Berzelius, hyposulphindigotic acid is also formed when indigo is dissolved in fuming sulphuric acid. Indigo-blue dissolves in cold sulphuric acid, first with a yellow colour, which afterwards becomes green, and finally of a beautiful blue (Housmann, Journ. de Phys. 1788; March, Chevreul). From the solution, while still yellow, undecomposed indigo-blue may be precipated by water; the yellow colour changes to blue in a few hours in a closed vessel, since sulphophœnicic acid is formed, which is gradually converted into sulphindigotic acid. When indigo is more strongly heated with sulphuric acid, sulphurous anhydride is evolved, and a brown oily liquid formed (Döbereiner). Liquid sulphurous anhydride does not act upon indigo (Bussy). Phosphoric anhydride and hydrated phosphoric acid are without action upon indigo; also concentrated hydrochloric acid. (Döbereiner.)

12. Indigo-blue is but slightly attacked by prolonged boiling with dilute *potash*; when the boiling point has reached 100°, the indigo is completely decomposed, whilst no gas is given off, and only traces of ammonia and phenylamine are evolved with the aqueous vapour (Fritzsche). According to Gerhardt (Rev. scient. x. 371), indigo-white and isatate of potassium are formed in this reaction:

$$\underset{\text{Indigo-blue.}}{3C^8H^5NO} + KHO + H^2O = \underset{\text{Indigo-white.}}{C^{16}H^{12}N^2O^2} + \underset{\text{Isatate of potassium.}}{C^8H^6KNO^3}$$

According to Fritzsche, a yellowish-red solution is first formed, on which a dark coloured substance floats, and from which yellow crystals of chrysanilate potassium are separated by continued boiling; on cooling, it solidifies into a crystalline mass, consisting principally of chrysanilate of potassium. The crystalline mass, when water is poured over it, immediately yields indigo-blue (in the same state as from the indigo-vat); the filtered solution also continues to deposit indigo-blue when exposed to the air. According to Gerhardt, Fritzsche's chrysanilic acid is nothing but a mixture of isatin, indigo-white, and perhaps also other products resulting from the further action of the potash. The indigo-blue is formed by oxidation of the indigo-white.

Indigo-blue fused with *hydrate of potassium* yields first isatic acid, as above, then phenylcarbamic acid resulting from the decomposition of the latter. (Gerhardt.)

$$\underset{\text{Isatic acid.}}{C^8H^7NO^3} + H^2O = \underset{\text{Phenyl-carbamic acid.}}{C^7H^7NO^2} + CO^2 + H^2,$$

and by further decomposition, salicylic acid (Cahours) and phenylamine (Fritzsche):

$$\underset{\text{Phenyl-carbamic acid.}}{C^7H^7NO^2} + H^2O = \underset{\text{Salicylic acid.}}{C^7H^6O^3} + NH^3$$

$$\underset{\text{Phenyl-carbamic acid.}}{C^7H^7NO^2} = \underset{\text{Phenyl-amine.}}{C^6H^7N} + CO^2$$

13. Indigo-blue placed in contact with water, an *alkali*, and a *deoxidising substance*, becomes at first coloured green, and is then converted into indigo-white, which forms a yellow solution with alkalis. In this reaction, water is decomposed, the hydrogen being used in the formation of indigo-white, *e. g.* with *stannous oxide :*

$$\underset{\text{Indigo-blue.}}{2C^8H^5NO} + SnO + H^2O = \underset{\text{Indigo-white.}}{C^{16}H^{12}N^2O^2} + SnO^2$$

The following substances react in a similar manner: phosphorus, phosphorous acid, sulphurous acid, sulphydric acid, potassium-amalgam, sulphide of potassium, sulphide of sodium, sulphide of arsenic, sulphide of antimony, zinc, tin, iron, ferrous, stannous, and manganous oxides, grape-sugar, and substances undergoing fermentation or putrefaction, as sugar, gluten, urine, woad, madder. Warm putrid urine dissolves indigo-blue, the ammonia-compound of indigo-white being formed. According to Löwenthal, on the contrary (J. pr. Chem. lxx. 463), this reduction of blue to indigo-white is not produced by salts of sulphurous or phosphorous acid, by sulphide of potassium, sulphide of calcium, manganous salts, or arsenite of sodium; but indigo-blue dissolved in sulphuric acid is reduced to indigo-white, when mixed with excess of acid carbonate of potassium or sodium, and then treated with sulphydric acid. Löwenthal is of opinion that indigo-white is not indigo-blue *plus* hydrogen, but indigo-blue *minus* oxygen.

Testing and Valuation of Indigo.—Commercial indigo occurs in small lumps or cubic loaves of a violet-blue colour; when of good quality it is very light; assumes a coppery aspect when rubbed with a hard polished body; and is free from flaws or cavities traversed by brown or whitish veins. The best sorts are light enough to float on water.

External characters, however, give but very uncertain indications of the amount of real colouring matter contained in a sample of indigo; hence it becomes necessary to resort to chemical methods of estimating the amount of pure indigo-blue. Good sorts of indigo contain about 60 per cent., but the proportion is often much reduced by fraudulent admixture of foreign substances, such as sand, vegetable mould, powdered lead, starch, &c. Some foreign matters are also unavoidably introduced in the process of manufacture.

The indigo is first dried over the water-bath to estimate the hygroscopic water; which, in samples not fraudulently moistened, varies from 3·5 to 6 per cent. The dried indigo is then calcined in a platinum crucible to determine the amount of ash. Good indigo generally yields from 7 to 10 per cent. The presence of sand, lead-powder, &c., may then easily be detected by washing the ash with water.

The presence of starch, sometimes coloured with iodine, is indicated by the pale colour, greater density, and friability which it imparts to the lumps of indigo. It may be further detected by treating the indigo with slightly alkaline water, neutralising the filtered liquid with a few drops of acid, and testing with iodine.

The older methods of estimating the proportion of real indigo-blue in commercial indigo depend, for the most part, on the decoloration produced by chlorine and other oxidising agents.

1. *With chlorine water.*—A weighed quantity of the finely pulverised indigo is added by small portions to a measured quantity of a saturated aqueous solution of chlorine, as long as it dissolves with yellow colour, and the quantity thus dissolved is ascertained by weighing the residue. A similar trial is then made with perfectly pure indigo-blue,

and a comparison of the two results gives the proportion of colouring matter in the sample of commercial indigo under examination. As the strength of the chlorine-water alters very quickly, it cannot be titrated long beforehand. (Berzelius.)

2. *With chloride of lime.*—The indigo is first dissolved by digestion for five or six hours at 50° or 60° with fuming sulphuric acid; the solution is thoroughly mixed with distilled water, and poured into a graduated burette, and from this vessel it is added drop by drop to a measured quantity of aqueous chloride of lime, till the blue colour just becomes permanent. A similar experiment being then made with an equal weight of pure indigo blue, the colouring power of the two samples is in the inverse ratio of the quantities of the blue solution consumed in the two experiments. (Schlumberger, Bull. Soc. industr. de Mulhouse, vol. xv.)

3. With *hydrochloric acid and chlorate of potassium.*—1 grm. of finely pulverised indigo is digested for some hours with 10 grms. of fuming sulphuric acid, agitating from time to time to assist the solution. The liquid is then poured into a basin containing a kilogramme of water, 50 grms. of strong hydrochloric acid are added, and the liquid is heated to the boiling point. On the other hand, 0·25 grm. of chlorate of potassium is dissolved in 100 grms. of water; and the solution is poured into a graduated burette, and added drop by drop to the boiling indigo solution till the blue colour changes to red-brown. The richness of the sample of indigo is directly proportional to the quantity of chlorate consumed. (Bolley, Ann. Ch. Pharm. lxxv. 242.)

4. With *sulphuric acid* and *acid chromate of potassium.* The mode of proceeding is the same as that just described; 10 grms. of pure indigo-blue prepared by Fritzsche's method require for decoloration exactly 7½ pts. of the acid chromate. (Penny, Chem. Soc. J. v. 297.)

All these methods are liable to the objection that it is difficult to institute an exact comparison between the different shades of colour resulting from the oxidation of the indigo in different cases, the pure green tint thus produced in solutions of pure indigo-blue giving place to a dirty olive or brownish-green when crude indigo is used, in consequence of the impurities contained in it. Moreover, in dissolving indigo in strong sulphuric acid, it is scarcely possible to avoid the formation of sulphurous acid, the presence of which will of course raise the apparent percentage of indigo-blue in the sample. By employing these methods indeed, it is common to find, in a good sample of indigo, more than 80 per cent. of pure indigo-blue, whereas the best qualities seldom contain above 60 per cent., and average qualities not more than 40 to 50 per cent.

The following methods, which depend upon the reduction instead of the oxidation of the indigo, give more exact results.

5. With *Protosulphate of Iron.*—A weighed quantity of the finely pulverised indigo is well mixed with an equal weight of pure lime previously slaked with water. The mixture is poured into a stoppered bottle of known capacity, and the mortar is well rinsed with water, which is added to the rest. The bottle is now heated in a water-bath for several hours, and a quantity of finely-powdered sulphate of iron is added; the bottle is then filled up with water; the stopper is inserted; and, after the contents have been well shaken, the whole is left at rest for several hours, till the indigo is reduced and the sediment has sunk to the bottom. A portion of the clear liquor is then drawn off with a siphon, and the quantity of liquid having been accurately measured, it is mixed with an excess of hydrochloric acid, and the precipitate, after having been oxidised (by exposure to the air), is collected on a weighed filter, and washed with water. Lastly, the filter with the indigo-blue is dried at the heat of the water-bath, and weighed, and the weight of the filter having been subtracted from that of the whole, the weight of the indigo-blue is ascertained. Suppose, for example, that the whole quantity of liquid was 200 measures, and that 50 measures have been drawn off, yielding 10 grains of indigo-blue; then the total quantity of indigo-blue in the sample is 40 grains. For 60 grains of indigo it is necessary to take from 1 lb. to 2 lbs. of water. This method, though rather tedious, gives better results than any of the preceding. The quantity of indigo-blue indicated by it is usually somewhat less than the actual quantity contained in the sample.

6. With *stannous chloride.*—The tin-solution is titrated with a solution of pure indigo-blue, prepared by dissolving the substance dried at 210°–230° C. (410°–446° F.) in 16 pts. of strong sulphuric acid, with addition of pounded glass to divide the indigo and facilitate the solution. The indigo-solution thus obtained is diluted with water, till a litre of it contains exactly 1 grm. of indigo-blue. The indigo to be examined is then dissolved in a similar manner, and the titrated tin-solution is added to it from a burette till the blue colour changes through green to light-yellow. Iron, if present in the indigo, must first be removed by digestion in hydrochloric acid, with addition of pounded glass. (E. Mulder, Scheik. Onderz. iii. [1] 37; Jahresber. 1860, p. 613.)

7. With *zinc.*—A solution of indigo in sulphuric acid is dilute with water and hydrochloric acid, and decolorised by zinc in an atmosphere of carbonic anhydride. A

measured volume of this solution is then introduced into a graduated tube filled with air or oxygen-gas, and the volume of oxygen absorbed is read off after a few hours. A similar experiment is then made with pure indigo-blue, and the value of the commercial sample is determined by comparison of the results.

INDIGO-BROWN. (Chevreul, Ann. Chim. lxvi. 5; Berzelius, *Lehrb.* iii. 685; Gm. xiii. 48.)—A brown substance of uncertain composition, existing together with indigo-blue, indigo-gluten, and indigo-red, in all kinds of commercial indigo. To obtain it, the indigo-gluten is first removed by treating the indigo with dilute sulphuric, hydrochloric, or acetic acid, and then with boiling water. On digesting the residue in hot strong caustic alkaline lye, the indigo-brown dissolves, together with a small portion of indigo-blue, forming a dark-brown, almost black solution, from which, after filtration, the indigo-brown may be precipitated by an acid. The precipitate contains a considerable quantity of indigo-blue, from which it may be freed for the most part by dissolving it in carbonate of ammonium, evaporating the filtrate to dryness, dissolving the residue in water, filtering from the undissolved portion, consisting chiefly of indigo-blue, and precipitating the filtrate with sulphuric acid.

Indigo-brown thus prepared forms a dark brown transparent resin, almost tasteless, and quite neutral. By dry distillation, it yields ammonia and an empyreumatic oil. It is decomposed by nitric acid and by chlorine. It unites both with acids and with bases. With the *alkalis*, it forms dark brown compounds, easily soluble in water. The *baryta-compound* is sparingly soluble, and the *lime-compound* insoluble. By boiling the alkaline compounds with lime in excess, the indigo-brown may be separated and rendered insoluble. This is perhaps one of the uses of lime in the indigo-vat (pp. 251, 252).

Indigo-brown bears a considerable resemblance to Schunck's indihumin (p. 264), one of the products of the decomposition of indican.

INDIGO-GLUTEN. This substance is extracted from crude indigo by treating it with dilute sulphuric, hydrochloric, or acetic acid, then with boiling water, and remains on evaporating the solution as a yellow, transparent extract, soluble in spirits of wine, easily soluble in water, less soluble in acid liquids. Its taste is like that of the extract of meat. It yields by dry distillation much ammonia and a fœtid oil, and behaves in most respects like ordinary vegetable gluten.

INDIGO-GREEN. Berzelius obtained a green substance by adding potash in small portions to an alcoholic solution of an alkaline hyposulphindigotate, till it became green, washing the precipitate with a little alcohol, decomposing it with oxalic acid, freeing the filtrate from oxalic acid by trituration with a little carbonate of calcium, then filtering and evaporating to dryness. The green solid residue thus obtained dissolved easily in water, forming a green solution, which, when mixed with lime-water, became yellow on exposure. It formed a green precipitate with acetate of lead, none with mercuric chloride or tincture of galls. (Berzelius.)

Chevreul also obtained a green substance from indigo, but it appears to have been merely indigo-brown mixed with a little indigo-blue.

INDIGO-PURPLE. See SULPHOPHŒNICIC ACID (p. 260).—The preparation of a "purple-blue" from indigo for dyeing is described by L. and E. Boilley (Dingl. pol. J. clix. 318), and has been patented in this country by Johnson (Rep. pat. Invent. Dec. 1860). It probably consists of sulphindigotate or sulphophœnicate of sodium. To prepare it, finely pulverised indigo is added to twenty times its weight of acid sulphate of sodium in the state of fusion, and the mixture is heated and stirred till a sample colours water violet. The paste thus produced is then intimately mixed with 70 to 80 times its weight of water; and the colouring matter is precipitated by common salt (2 lbs. to 1 lb. of the paste) and washed with water containing that salt. After drying, it forms a mass of interlaced silky crystals having a coppery lustre. (For further details, and specimens of fabrics dyed with this preparation, see Rép. Chim. app. 1860, p. 215.)

INDIGO-RED. A red substance occurring, together with indigo-gluten and indigo-brown, in commercial indigo. It was first noticed by Chevreul, afterwards more fully examined by Berzelius.

The indigo-gluten and indigo-brown having been removed in the manner already described, the residue is exhausted with boiling alcohol of specific gravity 0·83. A dark-red solution is then obtained which, when filtered and distilled, deposits indigo-red as an amorphous blackish-brown powder quite insoluble in water and in alkaline liquids. By distillation in a vacuum, it yields a white crystalline sublimate (the so-called colourless indigo-red, as well as unchanged indigo-red. Strong sulphuric acid dissolves it, forming a dark-yellow solution, which deposits nothing on addition of water. The dilute solution is decolorised by wool, which at the same time acquires a dirty yellowish-brown or red colour.

When the fresh leaves of *Polygonum tinctorium* are exhausted with ether, and part of the ether is distilled off, indigo-blue separates out; and on evaporating the remaining solution to dryness, and exhausting the residue with alcohol, filtering from a slight brown residue, again evaporating to dryness, and exhausting the residue with hot water, which extracts a little yellow colouring matter, a hard brittle friable resinous substance separates of a fine red colour, and probably agreeing essentially with the red of common crude indigo. It is insoluble in *water*, slightly soluble in *potash*, *ammonia*, and *acetic acid*, easily in *alcohol* and *ether*. The alcoholic solution turns red on addition of *baryta-water*, *lime-water*, *basic acetate of lead*, or *nitrate of silver*, and dark red with *stannous chloride*. With solution of *alum* it forms a beautiful red lake, not acted upon by alkaline carbonates.

The indigo obtained from the flowers of *Tankervillia cantonensis* contains a red substance, soluble in alcohol, but insoluble in water and in ether.

For further details respecting these indigo-reds, which are probably identical in the main with Schunck's indirubin (p. 268). See *Gmelin's Handbook*, xiii. 45.

INDIGO-SULPHURIC ACIDS. When indigo-blue is macerated in fuming sulphuric acid, heat is evolved, and a deep-blue solution is formed, called *sulphate of indigo*, *Saxony* or *composition-blue*, containing sulphindigotic acid, $C^8H^5NO.SO^3$. The liquid has a deep-blue colour, and may be diluted with water without becoming turbid; if, however, the sulphuric acid is not in excess, there generally remains a purple powder, consisting of sulphophœnicic acid, $2C^8H^5NO.SO^3$, insoluble in dilute acids, but soluble, with blue colour, in pure water. According to Berzelius, there is also formed a third acid, called hyposulphindigotic acid, which has not been analysed. The indigo-blue cannot be recovered from these acids by any known methods. Their solution loses its colour after a while, and is instantly turned yellow by a small quantity of nitric acid: this reaction is used in qualitative analysis for the detection of nitric acid.

Hyposulphindigotic acid. *Hyposulphocærulic acid.* To isolate this acid, the alcoholic solution of its ammonium-salt, obtained in the manner presently to be described (see SULPHINDIGOTIC ACID), is mixed with an alcoholic solution of acetate of lead; the whole is completely precipitated by addition of a little ammonia, and the precipitate is suspended in water and decomposed by sulphydric acid. A yellow liquid is then obtained, which, on exposure to the air, becomes blue, and is converted into hyposulphindigotic acid. By evaporating this solution, the acid is obtained as an amorphous mass, which becomes moist in contact with the air, dissolves readily in water, and reacts like sulphindigotic acid with sulphydric acid, zinc, iron, and charcoal.

The hyposulphindigotates resemble the sulphindigotates in many respects, but are distinguished by their solubility in alcohol of 84 per cent. When gently heated, they give off sulphurous anhydride without changing colour; at a higher temperature, they turn green and yield a sublimate of sulphite of ammonium.

The *ammonium-*, *potassium-* and *sodium-salts* are obtained by steeping wool dyed with sulphate of indigo in solutions of the corresponding alkaline carbonates, evaporating the resulting solutions to dryness, and exhausting the residues with alcohol, which takes up only the hyposulphindigotates.

The *aluminium-salt* resembles the corresponding salt of sulphindigotic acid.

The *barium-salt* is obtained by precipitating the potassium-salt with carbonate of barium, in dark-blue flocks, very soluble in pure water; the solution, when evaporated, deposits films having a coppery lustre.

The *calcium-* and *magnesium-salts* are very soluble in water and in alcohol.

The *lead-salt* is obtained by precipitating an alcoholic solution of the ammonium-salt with alcoholic acetate of lead. It is a blue powder, which dissolves slowly but completely in water: it is sparingly soluble in alcohol, and has an astringent taste.

Sulphindigotic Acid. $C^8H^5NO.SO^3$. *Sulphate of indigo*, *Soluble blue indigo*, *Sulphindylic acid*, *Sulphocærulic acid.*—Indigo may be dissolved in strong (monohydrated) sulphuric acid (SH^2O^4), as well as in the fuming acid (which contains sulphuric anhydride in solution), but it requires 15 pts. of the former, and only 6 pts. of the latter; moreover, the solution in common sulphuric acid requires the aid of heat, which gives rise to the formation of sulphurous acid; it may, however, be facilitated by triturating the indigo with pounded glass so as to divide the particles.

The acid solution is diluted with from 30 to 50 times its bulk of water; the liquid is filtered from the precipitated sulphophœnicic acid; the filtrate is digested at a gentle heat with wool or woollen stuff (previously prepared by washing, first with soap and then with water containing 1 per cent. carbonate of sodium, and finally with pure water), until no more colouring matter is taken up, the excess of sulphuric acid remaining in solution. The wool, dyed blue by sulphindigotic and hyposulphindigotic acids, is washed with water till the latter no longer becomes acid, and digested with water containing a little carbonate of ammonium; the blue solution is poured off from the decolorised wool, and evaporated to dryness at 50°; and the residue is exhausted with alcohol of 83 per cent., which dissolves the hyposulphindigotate of ammonium, and leaves the sulphindigotate. The latter is dissolved in water, and precipitated by acetate of lead; the dark-blue precipitate is washed with water, then suspended in water, and decomposed by sulphydric acid; and the yellow or colourless solution, which turns blue on exposure to the air, is evaporated to dryness at 50° (Berzelius). According to Joss, sulphindigotate of ammonium is not effectually separated from the hyposulphindigotate by alcohol; it is better, therefore, to digest the indigo-solution with wool only so long as it forms a precipitate with acetate of barium, by which hyposulphindigotic acid is not precipitated.

Properties.—Sulphindigotic acid forms a solid mass having a peculiar agreeable odour and an acid taste; it has a weak but decided acid reaction (Joss). It becomes moist in the air, and is very soluble in *water* and in *alcohol*. It is separated from its aqueous solution by wood-charcoal, and with greater facility by blood-charcoal, but may be extracted from the charcoal by alkaline carbonates.

Wool is dyed by the aqueous acid, but not by its salts, unless an acid is added, a comparatively weak acid, such as acetic acid, being sufficient for the purpose. Boiling water and alcohol deprive the wool of only a portion of its colour, but alkalis remove it entirely (Berzelius). Sulphindigotic acid is completely decolorised by woollen stuffs; silk fabrics do not deprive it of all its colour; linen and cotton take up very little. Silk dyed with it is deprived of its colour by soap, but not by water. (Bergmann.)

Decompositions.—1. Sulphindigotic acid yields by dry distillation sulphurous anhydride, sulphite of ammonium, much water, and a little empyreumatic oil. No vapours of indigo-blue are evolved, but the sublimed sulphite of ammonia dissolves in water with a blue colour, having carried over a little of the undecomposed acid. The carbonaceous residue burns with difficulty, but completely. The sulphindigotates also do not yield any sublimate of indigo by dry distillation (Berzelius).—2. Sulphindigotic acid is decomposed by exposure to sunlight.—3. *Chlorine* produces a quantity of brown resin in the solution of the acid, and only a little chlorisatin and dichlorisatin (Erdmann, *J. pr. Chem.* 19, 355).—The blue colour of the acid is changed to green by *chloride of lime* (Schlumberger), and to reddish-brown by *chlorate of potassium* and *hydrochloric acid* (Bolley).—4. Sulphindigotic acid is decomposed by *nitric acid.* When the barium-salt is decomposed by boiling with concentrated nitric acid and the solution diluted and filtered, it is not precipitated by chloride of barium (Berzelius).—5. The solution of sulphindigotic acid, heated with *chromate of potassium*, becomes ochre-yellow (Penny); mixed with *permanganate of potassium*, it becomes first green and then brownish-yellow (Elbers, Mohr); when heated with *ferric salts*, it is decolorised as by nitric acid (Wöhler, Ann. Ch. Pharm., xxxiv. 235). These reactions are used for the valuation of commercial indigo (p. 255).—6. *Deoxidising substances* reduce sulphindigotic acid to a compound derivable from indigo-white, and change the colour of the solution to yellow. *Zinc* or *iron* filings dissolve in the solution without disengagement of hydrogen, yielding a blue liquid, which, however, is decolorised by excess of acid: the solution quickly recovers its blue colour on exposure to the air. *Sulphydric acid* does not decolorise the solution at ordinary temperatures; but on heating the liquid to 60°, it deposits sulphur and becomes colourless. The decoloration is prevented by the presence of free acids. If the solution containing excess of sulphydric acid is evaporated in a vacuum over slightly moistened potash, a dark-yellow viscid residue is obtained, which becomes moist and dark-blue on exposure to the air. The solution of sulphindigotic acid is likewise decomposed by *stannous chloride.* (For further details on these reductions, see *Gmelin's Handbook*, xiii. 60.)

Sulphindigotates. $C^8(H^4M)NO.SO^3$.—These salts are formed by direct combination or by double decomposition. They cannot be obtained crystallised; they are dark blue, with a peculiar coppery lustre, and taste feebly saline and decidedly of indigo. The alkaline sulphindigotates are slightly soluble in cold water, and more readily in hot water; the solution is blue by reflected, and red by transmitted light.—The sulphindigotates are more readily decolorised than the free acid, by all substances which reduce indigo-blue, especially in the presence of free alkalis. *Protosulphate of iron* does not reduce a neutral sulphindigotate, even on warming; not even when as much alkali is added as is necessary to precipitate the protoxide of iron; but the slightest excess of alkali produces immediate decoloration, and on the addition of enough acid to neutralise the alkali, the blue colour is restored. *Sulphide of potassium* or *calcium* decolorises the solutions of the sulphindigotates, part of the sulphide being converted into sulphate. The reduced solution appears yellow when neutral, and burnt-yellow when alkaline. The neutral solution leaves, when evaporated in vacuo, a dark dry residue, which appears dark yellow when pulverised, and becomes blue on exposure to the air for several days. The solution turns blue on exposure to the air.

Ferric and *cupric salts* instantly turn the solution blue, and are converted into salts of the lower oxides. The solution reduced by *stannous chloride* deposits, on exposure to the air, a white powder, which is a mixture of stannic oxide and a product of decomposition which becomes green on exposure to the air.

Sulphindigotates, when heated, give off water without melting. When strongly heated, they decompose, evolving free ammonia, carbonate of ammonium, cyanide of ammonium, a trace of volatile oil, and afterwards of carbonic anhydride, whilst a residue of metallic sulphide is left.

Sulphindigotate of Ammonium is prepared by the process described on page 258 (Berzelius); or by precipitating sulphindigotic acid, which should not be too dilute, with ammonia or a salt of ammonia (Crum). It reacts similarly to the potassium-salt. It melts when heated and swells up, but is not decomposed, even by a pretty strong heat, and although it assumes a charred appearance, still dissolves completely in water, forming a blue solution. When more strongly heated, it yields a sublimate of sulphite of ammonium (Berzelius.) It dissolves in from 40 to 50 parts of cold water, and in a much smaller quantity of hot water (Crum), and is precipitated from the solution by the alkaline sulphates and some other salts, but much less completely than the potassium-salt. It is not soluble in alcohol. (Crum, Berzelius.)

Sulphindigotate of Aluminium is readily soluble in water, and dries up like the other sulphindigotates on the evaporation of the solution. Sulphindigotate of potassium, mixed with a salt of aluminium and a little ammonia, throws down a dark blue pulverulent basic salt, becoming blackish-blue when dried. It gives up all its acid to an excess of alkali. (Berzelius.)

Sulphindigotate of Barium is precipitated in dark blue flakes, on mixing the potassium-salt with chloride of barium (Crum, Berzelius). It dissolves slightly in cold water with a bluish colour; more abundantly in hot water, imparting to it a dark colour. Owing to the great affinity of baryta for sulphindigotic acid, this salt is formed when hyposulphindigotate of potassium is mixed, first with sulphuric acid, and then with chloride of barium; an excess of sulphate of barium is, however, necessary to the reaction, and hence the precipitate has a paler colour. Sulphate of barium already precipitated likewise forms with hyposulphindigotate of potassium, a small quantity of sulphindigotate, and becomes pale blue.

Sulphindigotate of Calcium is soluble in water, but insoluble in alcohol, which precipitates it in blue flocks.

Sulphindigotate of Lead is precipitated in dark blue flocks, slightly soluble in water on mixing neutral acetate of lead with sulphindigotate of potassium. Basic acetate of lead forms a light blue precipitate, which becomes darker when dry.

Sulphindigotate of Magnesium is very soluble in water, and is not precipitated by an excess of sulphate of magnesium.

Sulphindigotate of Potassium, $C^8H^4KNO.SO^3$. This salt is obtained: 1. By steeping wool dyed blue with sulphate of indigo, in a solution of carbonate of potassium, evaporating the solution, and treating the residue with alcohol, which extracts hyposulphindigotate of potassium. The residue is then treated with acetic acid and alcohol to remove the excess of carbonate (Berzelius).—2. Indigo-blue is treated with excess of sulphuric acid; and after the sulphophœnicic acid has been removed by filtration, the blue liquid is saturated with acetate of potassium; the resulting blue precipitate is thrown on a filter, and washed with acetate of potassium till the liquid which runs through begins to turn blue; the salt is then washed with alcohol to remove the acetate. (Dumas.)

Sulphindigotate of potassium in the dry state, forms a copper-coloured mass, yielding a blue powder; blue also by transmitted light. It rapidly absorbs moisture from the air.

When heated it does not melt or evolve any purple vapours; it is difficult to incinerate. According to Berzelius, it forms sulphopurpurate of potassium when heated with lime-water out of contact with the air; in presence of air, it forms salts of sulphoflavic, sulphofulvic, and sulphorufic acids.

Sulphindigotate of potassium dissolves in 140 parts of cold water, and in a much smaller quantity of boiling water, a portion separating out on cooling. The solution is of a dark blue colour, transparent only when viewed in thin layers; when held up before the light of the sun or of a candle, it appears scarlet. 1 part of the salt imparts a blue colour to 500,000 parts of water. Water containing 1 per cent. of acetate of potassium does not dissolve the salt in the cold; on heating, a portion dissolves and separates out in blackish flakes on cooling. It is readily dissolved by sulphuric acid, but is not soluble in concentrated hydrochloric acid (Crum); or in alcohol of specific gravity 0·80. (Berzelius.)

If an aqueous solution of sulphindigotate of potassium is mixed with a barium- or calcium-salt and carbonate or phosphate of sodium added, carbonate and phosphate of barium and carbonate of calcium are precipitated of a light blue colour, and phosphate of calcium of a deep blue colour. When the solution of sulphindigotate of potassium is mixed with acetate of lead and a solution of tannic acid, the precipitate of tannate of lead carries down all the colouring matter with it.

Sulphindigotate of potassium occurs in commerce as paste or dry powder, known as precipitated indigo, indigo-carmine, soluble indigo, or solid blue. It is used for dyeing linen of an azure-blue colour, and for producing very pure blue colours on wool.

Sulphindigotate of Sodium, also called indigo-carmine, resembles the potassium-salt, and is used for similar porposes, but is more soluble in saline solutions.

Sulphophœnicic acid, $2C^8H^5NO.SO^3$. *Indigo-purple, Phœnicin, Sulphopurpuric acid.*—This acid is formed when sulphuric acid is allowed to act upon indigo for a short time, or not in excess. To prepare it 1 pt. of indigo-blue is mixed with from 8 to 10 pts. of strong sulphuric acid, and kept for three days at a temperature of 50° or 60°; the solution is then diluted with water, and the precipitate of sulphophœnicic acid is filtered, washed with dilute hydrochloric acid, and dried in an oil-bath at 80°—100° (Dumas). Or powdered indigo is purified by boiling with dilute sulphuric acid, and then shaken up with from 7 to 8 pts. of strong sulphuric acid till the mixture becomes olive-green. The whole is then diluted with a very large quantity of water, and the precipitate of sulphophœnicic acid is collected on a filter and washed with water, which becomes more deeply blue in proportion as the sulphuric acid is removed. The last filtrates are evaporated to dryness. (Crum.)

As the extraction of the sulphophœnicic acid on the filter according to (1) is a very slow process, and when the greater part of the indigo-blue is converted into sulphophœnicic acid by the prolonged action of the sulphuric acid, water will no longer pass through the filter, the following method may be employed, which yields a more abundant, though less pure product. 1 pt. of powdered indigo is shaken in a flask with 10 pts. of strong sulphuric acid, till the blue colour which the indigo had at first lost is completely restored. For this purpose, from ten to twelve hours are requisite at 7°, three hours in the heat of the sun, 20 minutes at 38°, and a few moments at 100°. A large quantity of water is added; the solution is filtered; and the precipitate is taken from the filter and washed by decantation with water containing sufficient chloride of ammonium to prevent it from dissolving the sulphophœnicic acid. The solution of chloride of ammonium is allowed to run from the filter, and the precipitate is removed and suspended in a large quantity of water. After three days, the solution is poured off, and the water is renewed as long as sulphophœnicic acid continues to dissolve. The sulphophœnicic acid is then precipitated from the decanted solutions by chloride of potassium, and the precipitate is washed on a filter with water as long as the water continues to pass through. Sulphophœnicic acid thus prepared contains a little potassium-salt and a large quantity of earthy matter; after drying, it is no longer soluble in water. (Crum.)

Häffely triturates 1 pt. of finely powdered indigo with 20 pts. of common sulphuric acid; allows the whole to stand for some time, till a drop of the solution, which is at first blue, colours water or paper violet; and then mixes the solution with a large quantity of water: the action of the sulphuric acid is promoted by heating the whole to 40°. If less sulphuric acid is used, it must be more strongly heated; if only 3 pts. of sulphuric acid are employed for 1 pt. of indigo, the latter is not completely converted into sulphophœnicic acid. If fuming sulphuric acid is used, it is not easy to discover when the reaction is ended.

Properties.—Sulphophœnicic acid forms a blue mass or a purple-red powder, soluble in water, to which it imparts a blue colour. It dissolves readily, with blue colour, in sulphuric acid, especially in the fuming acid, being at the same time gradually converted into sulphindigotic acid. With a large quantity of soda-ley, it forms a yellow solution which turns blue if immediately mixed with sulphuric acid of 66° B.; but stronger sulphuric acid added after 24 hours, produces a whitish precipitate. (Gros-Renaud, Dingl. pol. J. 129, 288.)

The *sulphophœnicates* are precipitated from the aqueous solution of the acid by the addition of other salts. When dry they are red; their aqueous solutions are blue. They dissolve very sparingly in water, but more readily in alcohol. The solutions are reduced to yellow liquids by heating with sulphydric acid, by sulphate of iron and lime, or by caustic alkalis. The reduced solutions turn blue on exposure to the air, and on the addition of other salts, the salt of sulphophœnicic acid is precipitated unchanged.

The *ammonium-salt*, when heated, evolves sulphurous anhydride together with sulphite of ammonium, and a red vapour which yields a sublimate like indigo-blue. This sublimate is often bright green on the lowest edges, like the wing-cases of cantharides, and turns brown when burnished.

The *potassium-salt*, $C^{16}H^{9}KN^{2}O^{2}.SH^{2}O^{4}$ (?) is obtained by adding acetate of potassium to the aqueous solution of the acid. It is then precipitated in purple flocks, which must be washed, first with acetate of potassium, then with alcohol. It dissolves in 100 pts. of water.

The *sodium-salt* is obtained in like manner.

The solution of sulphophœnicic acid, even when very dilute, is precipitated by the salts of *calcium*, *magnesium*, *aluminium*, *iron*, *tin*, and *copper*.

Products obtained by decomposition of the Indigo-sulphuric acids.

The following products of the decomposition of these acids are described by Berzelius (*Lehrbuch der Chimie*, 4th Aufl. vii. 226); but their composition is very uncertain, and they require further examination:—

1. **Sulphoflavic acid.**—This acid is formed by heating sulphoviridate of potassium with lime-water in contact with the air.—To prepare it, sulphindigotate of potassium is heated with lime-water in an open vessel, until the solution acquires a pure red colour (if the action is too prolonged, it becomes yellow; if the access of air is kept under control, it is easier to hit the right moment). Carbonic anhydride is then passed through the liquid; the filtrate evaporated to dryness, and the green, brownish-yellow residue extracted with alcohol. The yellow solution is precipitated with acetate of lead; the lemon-yellow precipitate suspended in water and decomposed by sulphydric acid; and the solution filtered from the sulphide of lead is then left to evaporate. It forms yellow arborescent masses, having a strong acid taste and reaction. It is soluble in water and in alcohol; the solution forms with acetate of lead a lemon-yellow precipitate, insoluble in water.

2. **Sulphofulvic and Sulphorufic Acids.**—These acids are formed simultaneously with sulphoflavic acid. The residue, from which the sulphoflavic acid has been extracted by alcohol, is dissolved in water, and the bright-red solution is precipitated with basic acetate of lead. The pale-red precipitate is suspended in water, and decomposed with sulphydric acid, and the filtrate is evaporated to dryness. Absolute alcohol extracts from the residue, sulphofulvic acid, which, on evaporation, is deposited as a dark yellow, transparent mass, having the consistence of an extract; it forms a lead-salt, is readily soluble in water and in alcohol. The portion insoluble in alcohol is sulphorufic acid. This latter dissolves in water with a fine red colour, and, on evaporating the water, forms a dark red, opaque, amorphous mass, which tastes acid and strongly reddens litmus. The lead-salt is readily soluble in water and in alcohol.

3. **Sulphopurpuric Acid.**—This acid is formed by the action of alkalis upon sulphoviridic acid. 1 pt. of sulphindigotate of potassium is dissolved in 50 pts. of lime-water and heated in a covered vessel, till the solution, which has gradually turned purple red, does not become green again on cooling. After the whole has been allowed to cool in the covered vessel, the excess of lime is precipitated by carbonic acid; the filtrate is evaporated to dryness; and the residue treated with alcohol, which extracts a little sulphoflavic acid. The residue is dissolved in water, the purple-red solution precipitated with acetate of lead, and the precipitate suspended in water and decomposed by sulphydric acid; the filtered solution is then evaporated to dryness.

Sulphopurpuric acid forms a brown uncrystallised mass, dissolving in water with dark purple-red colour. The potassium-salt dissolves in water and imparts to it a dark purple-red colour, like that of permanganate of potassium. The precipitate produced by mixing the aqueous solution of the acid with acetate of lead, is slightly soluble in water, with a reddish colour; insoluble in alcohol. With excess of oxide of lead, a pale red salt is formed, which is insoluble in water.

4. **Sulphoviridic Acid.**—This is the first product of decomposition in the action of alkalis upon sulphindigotic acid.

1. To an alcoholic solution of an alkaline hyposulphindigotate, hydrate of potassium is added in small portions until it becomes green, and the green precipitate is washed on a filter with a little alcohol. The precipitate is decomposed by an aqueous solution of oxalic acid, filtered, and the filtrate is freed from excess of oxalic acid by triturating it with a little carbonate of calcium: it is then filtered and evaporated to dryness.

2. When a solution of hyposulphindigotate of barium is evaporated to dryness on a water-bath, it becomes green and yields a precipitate with basic acetate of lead, but not with the neutral acetate; and if the greyish-green precipitate is decomposed by sulphydric acid and the green filtrate evaporated to dryness, sulphoviridic acid is obtained as a dry, hard, gummy mass, having a strong acid reaction.

It dissolves very readily in water, and slowly, but completely, in strong alcohol; the solutions appear dark green by reflected light, and dark red by transmitted light. The aqueous solution mixed with lime-water becomes yellow in contact with the air. The *lead-salt* is somewhat soluble in water, imparting to it a greenish colour.

INDIGOTIC ACID. Syn. with NITROSALICYLIC ACID. (See SALICYLIC ACID.)

INDIGOTIN. Syn. with INDIGO-BLUE.

INDIGO-WHITE. $C^{16}H^{12}N^2O^2$. *White Indigo, reduced* or *deoxidised Indigo, Indigogen* (Gm. xiii. 93; Gerh. iii. 510).—A colourless substance, produced by the action of reducing agents on indigo-blue (pp. 251, 254), and differing from a double molecule of the latter ($C^{16}H^{10}N^2O^2$) by two atoms of hydrogen. Chevreul, who was the first to isolate it, supposed that it existed ready formed in indigoferous plants, and was converted into indigo-blue by oxidation; but Schunck has shown that this view is untenable, because indigo-white is soluble only in alkaline liquids, and the juice of plants is always acid. Moreover, if the indigo-white existed in the juice of these plants, it would be converted into indigo-blue by oxidation, on coming to the surface, which is not the case.

Preparation.—Commercial indigo, purified by boiling with hydrochloric acid, next with strong potash, and afterwards with alcohol, is mixed with freshly prepared hydrate of calcium (2 parts of quick-lime to 1 of indigo) and placed in a closed vessel with 150 parts of boiling water, after which sulphate of iron equal to one-third the weight of the indigo is added, and after the vessel has been closed, the whole is carefully shaken. After two days, the solution is decanted by means of a siphon into flasks filled with carbonic anhydride, and when the flasks are nearly full, they are completely filled with boiling dilute hydrochloric acid, corked up, and placed in a vessel containing cold water. The air is thus prevented from obtaining access to the indigo-white, which separates out in white crystalline flakes. After the indigo-white has settled down, the solution is drawn off with a wide siphon, and the deposit is thrown upon a filter, which is covered with a bell-jar, into which a stream of hydrogen or carbonic anhydride is passed. The filter is washed with cold water, which has been well boiled and then corked up. Indigo-white is very easy to wash, and if the deposit is allowed to stand for several days, it becomes so consistent that it may be washed in the air without becoming deeply coloured. After the contents of the filter have been washed, they are spread, while still moist, upon a glass plate and dried in a vacuum. When the indigo-white is dry, carbonic anhydride is allowed to flow into the receiver of the air-pump, in order that the pores of the dry mass may become filled with the gas (Berzelius, Dumas).—2. Three pts. of indigo-blue which have been purified by boiling, are digested for 24 hours with 5 pts. of hydrate of calcium, 4 pts. of sulphate of iron, and 120 pts. of water, in a closed flask filled with hydrogen, and the whole is frequently shaken till the deposit assumes a greenish-yellow and the solution a reddish-yellow colour. The lime is precipitated from the latter with carbonate of potassium, and the clear solution is decanted by means of a siphon filled with hydrogen, into a flask containing a mixture of hydrochloric acid and sulphite of ammonium. The thick white precipitate which is thus formed is filtered out of contact with the air, washed with water containing a little sulphite of ammonium, and dried at 100° in a stream of hydrogen. (Liebig.)

Properties.—Indigo-white thus prepared forms a coherent greyish-white mass having a faint silky lustre; if absolutely pure, it would probably be quite white. It is tasteless, inodorous, and does not change the colour of litmus. It is perfectly insoluble in *water*, and in such *acids* as do not decompose it, but dissolves in aqueous *alkalis*, in *alcohol*, and in *ether*, forming yellow solutions, which, when exposed to the air, turn yellow and deposit indigo-blue.

Decompositions.—1. When indigo-white is heated in a vacuum, a little water is evolved, a small quantity of indigo-blue sublimes, and a large carbonaceous residue is left (Berzelius).—2. When exposed to the *air*, and in contact with various *oxygen-compounds*, it takes up oxygen and is converted into indigo-blue. Freshly precipitated indigo-white turns blue immediately when shaken with water containing air, even if a free acid is present. After washing, and while still moist, it becomes purple through its entire mass on exposure to the air, unless it is rapidly dried. When dry, it requires several days' exposure to the air, to oxidise it completely, first becoming bright blue, and then dark blue through the entire mass. It cannot be preserved in sealed tubes, since the air contained in its pores is sufficient for its conversion into indigo-blue. Dry indigo-white exposed to the air at a gradually increasing temperature, suddenly becomes dark purple. When a *cupric salt* is added to an alkaline solution of indigo-white, a salt of the alkali, together with indigo-blue and cuprous oxide, are formed; the latter, on the addition of sulphuric acid, is decomposed into cuprous oxide, which dissolves, and a residue of metal.—3. Indigo-white precipitated from an alkaline solution by *nitric acid*, is turned blue by a slight excess of the acid, and then more completely decomposed (Berzelius). It dissolves instantly in *sulphuric acid*, and imparts to it a dark purple colour, which passes to blue on dilution. According to Berzelius, the indigo-white is oxidised, and part of the sulphuric acid converted into hyposulphuric acid.

Metallic Derivatives of Indigo-white.—Indigo-white dissolves readily in all aqueous *alkalis* and *alkaline earths*, also in the aqueous carbonates of ammonium, potassium, and sodium, and, according to Liebig, without depriving them of their alkaline reaction. The cold solutions are pure yellow, the warm and highly concentrated solutions brownish-yellow. When exposed to the air, they immediately deposit indigo-blue.

Indigo-white forms with *lime* a neutral compound, readily soluble in water, and a basic compound which is almost insoluble; this latter is precipitated when the solution of the more neutral body is digested with hydrate of calcium, or when indigo is digested with water, sulphate of iron, and excess of lime. The precipitate of gypsum and hydrated sesquioxide of iron, which is formed at the same time, may be readily suspended in water and separated by levigation. The basic compound is of a lemon-yellow colour, and very slightly soluble in water, to which it imparts a yellow colour. On exposure to the air, it first turns green, and then bright blue. (Berzelius.)

The alkaline solutions of indigo-white are precipitated by the salts of the *earth-metals* and *heavy metals*, yielding white precipitates, which turn blue in the air more quickly than indigo-white itself. The *magnesium-compound*, being slightly soluble, is partly thrown down as a white precipitate, and partly remains dissolved in the aqueous solution, to which it imparts a yellow colour; it turns blue on exposure to the air. The *aluminium-compound* is white, but rapidly turns blue on the filter; if it be then dried, it forms a dark blue crystalline powder which sparkles in sunshine; indigo-blue may be very readily sublimed from it, and a grey earthy residue then remains. (Berzelius.)

The *manganous compound* is dirty-green, and does not yield any sublimate of indigo-blue when dried in the air and heated. The *zinc-compound* is white, but rapidly turns blue on exposure to the air, and then yields a sublimate of indigo-blue when heated. The *lead-compound* is white and slightly crystalline, turns rapidly blue on exposure to the air, and if then heated, detonates slightly, and yields reduced lead. The *ferrous compound* is white, but quickly turns blue on exposure to the air; if it be *then* heated, it does not yield any sublimate of indigo-blue. The *cobalt-compound* is grass-green, and after drying in the air, does not yield any sublimate of indigo-blue when heated. Nitrate of *silver* produces with an aqueous solution of the potassium-compound a precipitate which is at first transparent brown, and then becomes black; it is not acted upon by the air, but when heated, produces a gentle explosion and yields a sublimate of indigo-blue and a residue of metallic silver. (Berzelius.)

INDIGO-YELLOW. A substance produced by heating hyposulphindigotate of calcium with lime-water, in contact with the air. It is a transparent yellow mass, with neutral reaction; swells up when heated, emitting an odour like that of burnt animal matter, and is slowly converted into a combustible cinder. It dissolves in water and in alcohol, forming yellow solutions. The aqueous solution is precipitated incompletely by neutral acetate of lead, completely by the basic acetate.

INDIHUMIN. A product of the decomposition of indican (p. 248) perhaps identical with indigo-brown. It is obtained but sparingly, and not on all occasions. It is a brown powder, containing 62·86 per cent. carbon, 4·71 hydrogen, 7·19 nitrogen, and 25·24 oxygen, agreeing nearly with the formula $C^{10}H^9NO^3$. It burns without melting when heated, is insoluble in water and in alcohol, but dissolves in aqueous alkalis, forming a brown liquid, from which it is precipitated by acids. It dissolves in boiling nitric acid, forming a yellow solution, which, on evaporation, leaves an orange-yellow residue.

INDIN. $C^{16}H^{10}N^2O^2$. (Laurent, Ann. Ch. Phys. [3] iii. 471.)—A compound, probably containing the elements of two molecules of indigo-blue, produced by the action of potash on isatyde, sulphisatyde, or disulphisatyde by heating isatan or isatyde:—

$$\underset{\text{Isatan.}}{C^{16}H^{12}N^2O^3} = \underset{\text{Indin.}}{C^{16}H^{10}N^2O^2} + H^2O.$$

$$\underset{\text{Isatyde.}}{2C^{16}H^{12}N^2O^4} = \underset{\text{Indin.}}{C^{16}H^{10}N^2O^2} + \underset{\text{Isatin.}}{2C^8H^5NO^2} + 2H^2O.$$

$$\underset{\text{Isatyde.}}{2C^{16}H^{12}N^2O^4} + 3KHO = \underset{\text{Indin-potassium.}}{C^{16}H^9KN^2O^2} + \underset{\substack{\text{Isatate of}\\\text{potassium.}}}{2C^8H^6KNO^3} + 3H^2O.$$

$$\underset{\text{Sulphisatyde.}}{2C^{16}H^{12}N^2SO^3} + 3KHO = C^{16}H^9KN^2O^2 + 2C^8H^6KNO^3 + H^2O + 2H^2S.$$

$$\underset{\text{Disulphisatyde.}}{2C^{16}H^{12}N^2S^2O^2} + 4KHO = C^{16}H^9KN^2O^2 + 2C^8H^6KNO^3 + KHS + 3H^2S.$$

It is most easily prepared by the action of potash on disulphisatyde. This substance is placed in a mortar, and potash poured upon it so that a stiff magma is formed, which is rubbed up for some time, and potash added drop by drop. When after five or six minutes the mass turns rose-coloured, alcohol is gradually added, and the whole is constantly stirred, until a dark rose-coloured paste is formed, which is diluted with alcohol, and filtered. The residue is washed, first with alcohol, and then with water. Since the indin thus obtained contains abundance of sulphisatyde, the water is removed from it by washing with alcohol, which is allowed to run through the filter; the indin is then taken from the filter and treated with very strong lukewarm potash, wherein it immediately forms a black solution, which after a few hours becomes thick with black needles of indin-potassium. (If the potash is too hot, the black colour disappears, and the indin is completely destroyed.) It is then diluted with absolute alcohol, and the solution removed with a pipette; the crystals are washed on a small filter with common alcohol, then with dilute hydrochloric acid, and finally with water; they are thus gradually reduced to red pulverulent indin. In order to obtain indin crystallised, the black crystals are dissolved in boiling absolute alcohol, and the boiling solution is mixed with hydrochloric acid; microscopic crystals then separate out on cooling.

Indin forms a deep rose-coloured powder or fine microscopic needles; insoluble in water, very sparingly soluble in *alcohol* and *ether*, even at the boiling heat. When heated, it swells up as soon as it begins to melt, yields a sublimate of needle-shaped crystals, and leaves a considerable quantity of charcoal. It dissolves with red colour in *sulphuric acid*, and is precipitated unchanged by water. With *nitric acid*, it yields nitrindin, and with bromine, dibromindin.

The analyses of indin, made at different times, do not agree very well together, the carbon varying from 71·55 to 72·09 per cent., and the hydrogen from 3·0 to 4·65; the nitrogen in one analysis was found to be 11·0 per cent. The formula $C^{16}H^{10}N^2O^2$ requires 73·3 C, 3·8 H, and 10·6 N. The differences arose, according to Laurent, from the presence of hydrindin, into which a portion of the indin had been converted by the further action of the potash.

Indin-potassium, probably $C^{16}H^9KN^2O^2$. This compound is formed in the preparation of indin as above described, and may be prepared in a state of greater purity by warming indin moistened with alcohol, and dissolving it in strong alcoholic potash. The black solution, if immediately taken from the fire, deposits black crystals, which must be freed from the liquid by decantation, rapidly washed with absolute alcohol, then laid upon paper, and dried in a vacuum on a porous tile. The crystals rapidly attract moisture from the air, and are resolved into potash and indin. The compound gives by analysis from 11·5 to 12·0 per cent. potassium, whereas the above formula requires 13·0 per cent. The analyses agree better with the formula $C^{16}H^{11}KN^2O^3$, which is that of the potassium-salt of an acid, related to indin in the same manner as isatic acid, $C^8H^7NO^3$, to isatin, $C^8H^5NO^2$.

Derivatives of Indin.

Dibromindin. $C^{16}H^8Br^2N^2O^2$. (Erdmann, J. pr. Chem. xxii. 265. Laurent, Ann. Ch. Phys. [3] iii. 371.)—Produced:—1. By the action of bromine on indin (Laurent). —2. By heating dibromisatyde (Erdmann).—3. By the action of bromine upon disulphisatyde. (Laurent.)

To prepare it, indin is treated with bromine, whereupon hydrobromic acid is evolved, and a violet-black powder is formed (Laurent). Or dibromisatyde is heated at a temperature not exceeding 220°, and dibromisatin and undecomposed dibromisatyde are removed from the products by treating them with boiling alcohol (Erdmann). Or bromine is poured upon disulphisatyde, whereupon hydrobromic acid and bromide of sulphur are evolved, and the soft brown mass thus formed is treated with ether, which extracts resin and an orange-yellow crystalline mass, and leaves dibromindin as a violet-black powder. (Laurent.)

Prepared according to 1 and 3, it is a violet-black powder; prepared according to 2, it is blackish red. It is slightly soluble in *alcohol* and in *ether*.

When dibromindin is heated between two platinum crucible-covers, the greater part chars; placed on glowing charcoal, it yields a sublimate of shining copper-coloured laminæ, which appear violet by transmitted light under the microscope. It blackens when treated with potash; if water is added and the whole boiled, the dibromindin gradually dissolves and forms a yellow solution, from which acids precipitate yellow flakes. When it is boiled with alcohol and solid hydrate of potassium, a blackish red solution is formed, from which water or hydrochloric acid precipitates violet-coloured dibromindin. (Laurent.)

Dichlorindin. $C^{16}H^8Cl^2$. (Erdmann, J. pr. Chem. xxii. 264.)—Produced from chlorisatyde by the action of heat, or by treating it with potash.

Chlorisatyde is heated to 200°, and the product is freed from chlorisatin and undecomposed chlorisatyde by boiling alcohol. Or, chlorisatyde is dissolved in warm potash, and allowed to cool: the mother-liquor is poured off from the deposit of chlorisatate of potassium, and mixed with acetic acid, which precipitates yellow chlorisatic acid. On subsequently heating the filtrate with hydrochloric acid, it assumes a deep orange colour, and deposits violet flakes of chlorindin, which are filtered from the hot solution.

Chlorindin forms a dirty violet powder, insoluble in water, hydrochloric acid, and *alcohol*. It dissolves in *potash*, forming a yellowish solution, with which hydrochloric acid gives a yellow precipitate, soluble with yellow colour in water.

Tetrachlorindin. $C^{16}H^{6}Cl^{4}N^{2}O^{2}$. (Erdmann, *loc. cit.*)—Produced from chlorisatyde by the action of heat below 200°, or by the action of potash. It resembles chlorindin.

Hydrindin. $C^{32}H^{22}N^{4}O^{5}$? (Laurent, Ann. Ch. Phys. [3] iii. 475.)—A compound produced by the action of alcoholic potash upon indin, isatin, isatyde, sulphisatyde, or disulphisatyde.

Preparation.—1. Indin moistened with alcohol is warmed with strong potash-ley till the solution, which is at first black, has become colourless, and the crystals of hydrindin-potassium, which separate out on cooling, are completely freed from potash by water.—2. When isatyde is treated with potash and a little alcohol, a beautiful rose-coloured solution is formed, which, when mixed with hydrochloric acid, and gently evaporated, becomes yellow, and deposits on cooling a mixture of isatin and hydrindin, from which the isatin is extracted by treating with a little boiling alcohol. —3. Sulphisatyde dissolves completely in gently heated potash, and on cooling, the potassium-compound of hydrindin sometimes separates out in beautiful small, pale-yellow crystals; sometimes, however, the solution solidifies into a mass of needles having a silky lustre. The whole is mixed with a large quantity of water, and the crystals are washed on a filter till all the potash is extracted. The filtrate mixed with hydrochloric acid still deposits a small quantity of hydrindin, together with a substance which is perhaps indin.

Hydrindin forms a white or pale-yellow powder, insoluble in *water*, slightly soluble in boiling *alcohol*, and separating from the solution on cooling, in small rhombic or six-sided needles.

Hydrindin carefully heated above 300°, turns violet-brown and gives off 2 at. water; the residue behaves with alcoholic potash like indin.—With boiling nitric acid it forms a violet powder similar to nitrindin.

Hydrindin contains, according to the mean of Laurent's analyses, 69·80 per cent. C, 4·85 H, and 10·70 N. The formula, $C^{32}H^{22}N^{4}O^{5}$, deduced therefrom by Laurent, which represents hydrindin as composed of 2 at. indin + $H^{2}O$, requires only 4·0 per cent. H, which is much below the analytical number. Gerhardt suggested the formula $C^{32}H^{22}N^{4}O^{4}.H^{2}O$, which requires 70·59 per cent. C, 4·41 H, and 10·29 N, and represents hydrindin as a hydrate of a double molecule of indin + 2 at. H. The formation of hydrindin by the action of potash on indin, &c. is more favourable to Laurent's than to Gerhardt's view, provided hydrindin is the sole product of the reaction; but in reality other products are formed at the same time, so that the formation of the more highly hydrogenised compound, hydrindin, may perhaps be compensated by that of one or more compounds containing a larger proportion of oxygen. The organic molecule, $C^{16}H^{12}N^{2}O$, associated with the elements of sulphuric acid in Schlieper's hydrindinsulphuric acid (p. 267) differs from indin by the substitution of 2 at. H for 1 at. O; but as the mode of formation of this molecule is altogether different from that of Laurent's hydrindin, it is probable that the two have little more in common than the name.

Hydrindin-potassium. $C^{32}H^{21}KN^{4}O^{5}.3H^{2}O$? When hydrindin is dissolved in warm aqueous potash, this salt separates out in short, brilliant, pale-yellow prisms or silky needles, containing, according to Laurent's analysis, 60·0 per cent. C, 4·3 H, 5·6 K, and 9·0 water of crystallisation; these numbers agree better with Laurent's formula above given, which requires 60·54 per cent. C, 4·27 H, and 6·18 K, than with that which corresponds to Gerhardt's formula of hydrindin, viz. $C^{32}H^{21}KN^{4}O^{4}.3H^{2}O$ which requires 62·11 C, 4·37 H and 6·34 K. The salt is decomposed by washing with water, leaving nothing but hydrindin.

Nitrindin. $C^{16}H^{8}N^{4}O^{6} = C^{16}H^{8}(NO^{2})^{2}N^{2}O^{2}$. (Laurent, Ann. Ch. Phys. [3] iii. 478.)—Produced by boiling indin or hydrindin with nitric acid. Isatyde and sulphisatyde probably also yield nitrindin when boiled with nitric acid.

It is a bright violet powder, insoluble in water, very slightly soluble in alcohol and ether.

It decomposes rather quickly when heated in closed vessels, and leaves a residue of bulky charcoal, which glows even out of contact with the air. It is gradually decomposed by boiling *nitric acid*. It dissolves in *potash*, forming a deep brown solution, from which hydrochloric acid throws down sometimes undecomposed indin, and sometimes yellow flakes, especially if the solution has been boiled. With *sulphite of ammonium* it behaves like indin. Ammonia does not act upon it.

INDINSULPHURIC ACID. $C^{16}H^{12}N^2S^2O^9 = (C^{16}H^{10}N^2O^2.SO^3).SH^2O^4$. (G. and A. Schlieper, Ann. Ch. Pharm. cxx. 24.)—An acid produced by the oxidation of hydrindinsulphuric acid (see below). The transformation may be effected by heating hydrindinsulphuric acid with a few drops of nitric acid, or by treating it with an alkaline of solution of ferricyanide of potassium or hypochlorite of sodium. The hydrindinsulphates are also converted into indinsulphates by exposure to the air, especially in alkaline solution, or by heating them with nitric or nitromuriatic acid. The mother-liquor obtained in the preparation of hydrindinsulphate of barium, treated with hot nitric acid, yields large quantities of the indinsulphate. The free acid may be obtained in the crystalline form by decomposing the barium-salt with sulphuric acid, and evaporating the filtrate. It has a red colour, is easily soluble in *water*, sparingly in *alcohol*, and is precipitated from the alcoholic solution by *ether*, in red flocks. The aqueous solution dyes silk and wool scarlet. Its colour is altered by *alkalis*, probably in consequence of a change analogous to the conversion of isatin into isatic acid. By *sulphydric acid* it is reduced to hydrindin-sulphuric acid:

$$C^{16}H^{12}N^2S^2O^9 + 2H^2S = C^{16}H^{14}N^2S^2O^8 + S^2 + H^2O.$$

Indinsulphuric acid is dibasic, and appears to form soluble salts with most bases. The salts when heated yield a crystalline sublimate of a fine red colour.

The *barium-salt*, $C^{16}H^{10}Ba^2N^2S^2O^9.2H^2O$, is obtained, by drenching the hydrindinsulphate with dilute ammonia, exposing it to the air, and stirring frequently, as a finely crystalline powder of a fiery carmine-red colour; or, by heating the mother-liquor of the hydrindinsulphate with nitric acid, as a light powder consisting of slender dark-red, brown needles. It is moderately soluble in pure water, insoluble in aqueous chloride of barium, alcohol, and cold hydrochloric acid and nitric acids. At 100° it gives off 6·45 per cent. water (calc. 2 at. = 5·89), and the dried salt yields by analysis 33·64 per cent. carbon, 2·02 hydrogen, and 26·27 to 26·74 baryta, the formula requiring 33·39 C, 1·74 H, and 26·60 Ba^2O.

The *potassium-salt*, $C^{16}H^{10}K^2N^2S^2O^9.5H^2O$, is obtained, by oxidising the solution of the hydrindinsulphate, by exposure to the air, or by means of ferricyanide of potassium, as a bulky carmine-coloured precipitate, perfectly insoluble in liquids containing potash. A hot solution of indinsulphuric acid mixed with excess of a potassium-salt, the chloride for example, deposits the indinsulphate on cooling in interlaced needles of a dark-red colour and almost metallic lustre, and so bulky that they nearly fill the liquid. The air-dried salt heated to 100° gave off, on the average, 14·24 and 14·34 per cent. water (calc. 5 at. = 14·85), and the remaining anhydrous salt gave by analysis 18·09 and 18·21 per cent. K^2O, the formula requiring 18·21 per cent.

The *silver-salt*, $C^{16}H^{10}Ag^2N^2S^2O^9$, is obtained by mixing a solution of the acid with excess of nitrate of silver, in small brown bulky needles yielding (at 100°) by analysis 29·39 per cent. C, 1·58 H, and 32·76 Ag; calc. 29·36 C, 1·53 H, and 33·02 Ag.

Hydrindinsulphuric acid. $C^{16}H^{14}N^2S^2O^8 = (C^{16}H^{12}N^2O.SO^3).SH^2O^4$. (G. and A. Schlieper, Ann. Ch. Pharm. cxx. 20.)—This acid, which may be derived from indinsulphuric acid by the substitution of 2 at. H for 1 at. O,* is produced by the action of sulphydric acid or sulphide of ammonium on indinsulphuric, or isatinsulphuric acid; also of zinc and hydrochloric or sulphuric acid on the latter, but not by the action of hydriodic acid.

Preparation.—A moderately concentrated solution of isatinsulphuric acid (1 pt. of the acid to 5 or 6 pts. water) is slightly supersaturated with ammonia, then mixed with half its bulk of sulphide of ammonium, and heated to boiling, the liquid then becoming brown from dissolved sulphur, and smelling strongly of ammonia. More sulphide of ammonium is then gradually added to the boiling liquid, till it smells permanently of sulphydric acid; and the boiling is continued (in a flask, to prevent oxidation) as long as a trace of ammonia escapes. The neutral pale-red solution filtered from the separated sulphur consists almost wholly of hydrindinsulphate of ammonium, which may be converted into the barium-salt by precipitation with chloride of barium, and from this the acid is obtained by decomposition with sulphuric acid.

Hydrindinsulphuric acid is obtained, by evaporation of its aqueous solution, as a colourless radio-crystalline mass, which becomes reddish when exposed to the air. It has a very sour taste, dissolves easily in *water*, less easily in *alcohol*, and is insoluble in *ether*.

The acid is dibasic; its salts are almost all soluble, and are easily converted into indinsulphates by oxidation, especially in alkaline solutions.

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* In the original memoir (p. 31), the two acids are said to be related to one another in the same manner as indigo-white and indigo-blue; but this statement is inconsistent with the formulæ.

The *barium-salt*, $C^{16}H^{12}Ba^{2}N^{2}S^{2}O^{9}.4H^{2}O$ (air-dried), is a light crystalline powder consisting of white shining scales. At 100° it gives off 11·68 per cent. water (calc. 11·37 per cent.), and the anhydrous salt yields by analysis 26·96 and 26·87 per cent. $Ba^{2}O$, the formula requiring 27·27 per cent.

Leucindin-sulphuric acid. $C^{16}H^{16}N^{2}S^{2}O^{10}$. (G. and A. Schlieper, Ann. Ch. Pharm. cxx. 33.)—This acid, which differs from the last by the elements of one molecule of water, is also produced by the action of sulphide of ammonium on isatinsulphuric acid. If in the process above described, the liquid, after filtration from the sulphur, be immediately mixed with excess of caustic baryta, instead of being evaporated, the whole of the ammonia then expelled by boiling, the excess of baryta removed by carbonic acid, and the clear yellowish solution strongly concentrated by evaporation, it deposits, after standing for a few days, white crystalline crusts of leucindin-sulphate of barium, which when recrystallised, forms hard, colourless, shining crystals containing $C^{16}H^{16}Ba^{2}S^{2}O^{10}$, with probably 5 at. water. They gave off 11·65 per cent. water at 100°, and 14·3 per cent. at 120° (mean 12·97); by calculation 5 at. = 13·1. The anhydrous salt gave by analysis (mean) 28·10 per cent. C, 3·85 H, and 22·14 $Ba^{2}O$; calculation 27·94 C, 3·78 H, and 22·27 $Ba^{2}O$.

By decomposing the barium-salt with sulphuric acid, and evaporating the filtrate, leucindin-sulphuric acid is obtained as a white crystalline mass, having a very sour taste, easily soluble in water, sparingly in alcohol. Its alkaline solutions are not reddened either by exposure to the air, or by treatment with oxidising agents. The solution of the barium-salt is not precipitated by nitrate of silver; but on adding ammonia, a white flocculent precipitate is formed, which turns brown when warmed; acetate of lead forms a red precipitate. The barium-salt evaporated down with hydrochloric or sulphuric acid, is converted into indinsulphate of barium; it is not altered by heating with potash.

INDIRETIN. $C^{18}H^{17}NO^{5}$. (Schunck, Phil. Mag. [4] xv. 29, 117.)—A compound, produced, together with indihumin, indirubin, and other products, by the action of dilute sulphuric acid upon indican (p. 248). It is a dark-brown shining resin, which at 100°–190°, contains on the average 66·04 per cent. C, 5·57 H, 3·83 N, and 24·56 O (calc. 66·05 C, 5·19 H, 4·28 N, and 24·48 O).—When *heated* on platinum foil, it melts, burns with a yellow, smoky flame, and leaves charcoal. By *dry distillation* it gives off strong-smelling vapours, and yields an oily distillate. It dissolves in *oil of vitriol* with brown colour, and chars when heated. With boiling *nitric acid*, it forms resin, and picric acid.—It dissolves easily in aqueous *alkalis*, and with brown colour in *ammonia*, being precipitated therefrom by *barium*, *calcium*, and *silver-salts*. It is precipitated from the alcoholic solution by *neutral acetate* of *lead*, and partially by *cupric acetate*.

INDIRUBIN. $C^{8}H^{5}NO$. (Schunck, *loc. cit.*)—A compound, isomeric with indigo-blue (p. 249), and perhaps identical with indigo-red (p. 257), obtained in small quantity by decomposition of indican, more abundantly from Indian woad-leaves, by immersing them in a boiling alkaline solution of stannous chloride, the liquid then depositing indirubin on exposure to the air. The product thus obtained is purified by dissolving it in alkaline stannous chloride, and treating it, after reprecipitation, with caustic soda, acids, and water, and then recrystallised from alcohol. It forms long, purple, metallic-shining needles, which appear red by transmitted light, and when heated volatilise in red vapours and sublime. In the impure state, it is a brown-red amorphous powder. Contains 72·78 per cent. C, 10·50 N, 4·16 H, and 12·56 O, agreeing with the formula above given. It dissolves with purple colour in *strong sulphuric acid*, and is partially precipitated therefrom by water. Cold *nitric* acid dissolves it with purple colour, but on applying heat, decomposition takes place, attended with formation of resin and picric acid. It is but slightly altered by a mixture of *chromate of potassium* and dilute *sulphuric acid*, even at the boiling heat. With *chlorine* under water, it forms a blue amorphous resin soluble in alcohol. Heated with *soda-lime*, it gives off an odour of benzoïn, together with alkaline vapours, which partly condense to needles. It is insoluble in aqueous alkalis, but dissolves easily on addition of *stannous chloride* or *grape-sugar*. From the yellow solution, acids throw down dirty yellow flocks, which acquire a purple colour on exposure to the air, and impart a fast purple dye to cotton-wool immersed in the liquid and afterwards exposed to the air. It is not precipitated from the alcoholic solution by ammoniacal *sugar-of-lead*. Its sulphuric acid solution imparts a fine colour to wool, cotton, and silk.

INDIUM. A metal recently discovered by F. Reich and Th. Richter (J. pr. Chem. lxxxix. 441) in the zinc-blende of Freiberg. Its spectrum is characterised by two indigo-coloured lines, one very bright and more refrangible than the blue line of strontium; the other fainter but still more refrangible, approaching the blue line of potassium. It was the production of this peculiar spectrum that led to the discovery of the metal. The ore, consisting chiefly of blende, galena, and arsenical pyrites, was roasted to expel sulphur and arsenic, then treated with hydrochloric acid, and the solution was evaporated to dryness. The impure chloride of zinc thus obtained, exhibited, when examined by the spectroscope, the first of the indigo lines above mentioned. The chloride was afterwards obtained in a state of greater purity, and from this the hydrate and the metal itself were prepared. The first line then came out with much greater brilliancy, and the second was likewise observed.

Indium has hitherto been obtained in very small quantity only, so that its properties have been but imperfectly studied. The metal itself is of a lead-grey colour, soft, very malleable, and marks paper like lead. It dissolves easily in hydrochloric acid, forming a deliquescent chloride. From the solution of this salt, it is precipitated by ammonia and potash as a hydrate, insoluble in excess of either reagent. Sulphydric acid does not precipitate it from acid solution. The oxide heated on charcoal with soda, yields a metallic globule, which when reheated oxidises to a yellowish powder. The compounds of indium impart a violet tint to the flame of a Bunsen's burner.

INDUCTION, ELECTRICAL. See Electricity (ii. 384, 451).

INDUCTION, MAGNETIC. See Magnetism.

INDUCTION, PHOTOCHEMICAL. See Light, Chemical action of.

INDYLE. Syn. with Indigo-blue. (Gerh. iii. 509.)

INFUSORIA. The following experiments on the influence of infusoria in exciting fermentation, have been made by Pasteur (Compt. rend. lvi. 416; Rép. Chim. p. 1863, p. 221). A quantity of tartrate of calcium mixed with a few thousandths of phosphate of ammonium and alkaline and earthy phosphates (either artificially prepared, or from the ashes of beer or of infusoria), was placed in a flat-bottomed bottle, the narrow neck of which was cemented to a bent glass tube; the bottle was then filled up with pure water, and the water heated to the boiling point, while the end of the bent tube was plunged into water likewise heated to boiling; by this means all the air in the solution was driven out. The surface of the water in the vessel into which the bent tube dropped was then covered with a thick layer of oil, and the apparatus was left to itself for twenty-four hours. Not the slightest trace of fermentation could then be perceived; but on quickly introducing into the bottle a small quantity of infusoria produced by spontaneous fermentation of tartrate of calcium, and immediately replacing the small quantity of water thereby dislodged, with water deaërated by boiling, and plunging the end of the tube below the surface of mercury so as completely to exclude the air, the infusoria multiplied rapidly in the deposit of tartrate, which soon disappeared completely, being replaced by a deposit consisting of the carcases of infusoria.

Hence it appears that the fermentation of the tartrate is determined by the presence of an animalcule living without free oxygen. If the bottle is filled up with aërated water, the tartrate ferments spontaneously, and the infusoria multiply quickly, removing the oxygen present down to the last trace, and replacing it by a slightly larger volume of carbonic anhydride. The ferment finds the nitrogen and phosphates required for its development in the albuminous matter present or the ammoniacal salts and phosphates introduced. The carbon is supplied by the tartaric acid. (See Fermentation.)

On the influence of infusoria on the germination of plants, see Lemaire, Compt. rend. 1863, Sept. 21; Rép. Chim. app. 1863, p. 371.

From experiments by Morrin (Compt. rend. xxxviii. 932; Jahresber. 1855, p. 649), it appears that the development of infusoria and algæ goes on only when they can obtain a supply of nitrogen already in the state of chemical combination, *e.g.* as evolved by decomposing animal matters, or in the form of ammonical salts. They grow in water which is in contact with atmospheric air continually renewed, but die if the air has been deprived of ammonia and organic matters by washing with oil of vitriol.

According to Salm-Horstmar (Jahresber. 1854, p. 145; 1855, p. 134), the green colouring matter of infusoria is optically identical with chlorophyll.

INFUSORIAL EARTH. The infusorial earth situated on the southern edge of the Lüneburg heath, near Ebsdorf, has been analysed by W. Wicke (Ann. Ch. Pharm. xiv. 292). It consists of two layers, the upper, which is from 10 to 18 feet thick, being light-coloured, and nearly white when dry, and the lower, which is 10 feet thick, or more, of a brownish-grey colour.

	Water.	Organic matter.	SiO^2	Ca^2CO^3	Fe^4O^3	Al^4O^3		
Upper . .	8·43	2·28	87·86	0·75	0·73	0·13	=	100·18
Lower . .	24·43		74·48	0·34	0·39	—	=	99·64

INK. Every liquor or pigment used for writing or printing is distinguished by the name of ink. Inks are of various colours, but the black and red are most in use, both for writing and printing. We shall first speak of *writing inks*, which consist either of a coloured and not too thin liquid, or a finely divided coloured precipitate suspended in a liquid.

1. **Black inks.**—Common black ink for writing is made by adding an infusion or decoction of nut-galls to a solution of copperas (ferrous sulphate). The infusion or decoction of the galls contains both gallotannic and gallic acids, both of which produce deep-black precipitates with ferric salts, but with ferrous salts, white precipitates which turn black by oxidation on exposure to the air. Moreover, gallic acid colours ferric salts of a much deeper black than gallotannic acid; hence it is advantageous to leave the infusion to itself for some time, either before or after mixture with the iron-salts, in order that the tannic acid contained in it may be converted into gallic acid (ii. 767, 768).

To retain the precipitate in suspension, and prevent it from forming a sediment, a certain quantity of gum is always added: the gum likewise gives a certain gloss to the ink. These are the essential ingredients of good writing ink, and any other colouring matters added, for the sake of cheapness, as substitutes for a portion of the galls, only impair its quality. Logwood is sometimes used, for the sake both of the tannin and the colouring matter which it contains.

To prevent ink from becoming mouldy, various substances are added to it, such as essential oils, finely bruised cloves, a few drops of phenic acid, and sometimes (but not advantageously) corrosive sublimate. The addition of an acid retards the conversion of the ferrous into ferric salt; the ink then remains thinner and pale while kept in the bottle, and becomes darker only as the writing dries.

The following are some of the numerous recipes for the preparation of black ink, calculated for 1,000 pts. of water:—

	a	*b*	*c*	*d*	*e*	*f*	*g*
Galls . .	225	187	133	125	66	62	31
Copperas .	75	73	55	24	22	31	19
Gum-arabic .	25	73	55	24	19	31	8

	h	*i*	*k*	*l*	*m*
Galls	50	174	50	60	42
Logwood . . .	—	—	100	20	21
Copperas . . .	32	87	16	20	21
Sulphate of copper .	—	—	—	—	5
Gum	9	43	47	20	16
Sugar	—	—	23	1000	
Vinegar . . .	125	135	—	—	—

Of the genuine inks (*a*—*g*), *a*, *b*, and *c* are too strong for ordinary use; *d*, *e* and *f* are perhaps the best; *g* would be somewhat too pale. The rest cannot be recommended, excepting for special purposes. Sulphate of copper deepens the colour of the precipitate, but renders it more compact and heavy, and therefore more apt to settle down. A certain quantity of sugar renders the ink more fluid, and permits the addition of a larger proportion of gum. It likewise renders the ink adhesive when dry, so that a copy of the writing may easily be taken off by laying a sheet of thin unsized paper, damped with a sponge, on the written paper, and passing lightly over it a flat iron very moderately heated: ink of this quality is called **copying ink.**

The so-called **alizarin-inks** (a mere commercial name, by no means implying that they contain the alizarin of madder) consist of common ink mixed with a little free sulphuric acid, which, like other acids, retards the oxidation of the ferrous precipitate (see IRON, OXIDES OF), so that the writing becomes black only after exposure to the air; the change being, perhaps, accelerated by the neutralisation of the sulphuric acid by the basic substances contained in the paper; the ink blackens very quickly when exposed to ammoniacal vapours. A certain quantity of sulphindigotic acid (p. 258), or its sodium-salt (indigo-carmine) is usually added, so that the ink may not appear too pale in writing. An ink of this kind may be prepared by exhausting 40 pts. by weight of nut-galls with 112 pts. water, and then adding 7 pts. copperas and ¼ pt. oxalic acid. At the same time, 1 pt. of finely pulverised indigo-blue is dissolved in 4 pts. fuming sulphuric acid; the solution after 24 hours is diluted with water, and mixed with a small quantity of carbonate of soda; the precipitate is collected, washed to remove the saline solution, then suspended in water; and this liquid is added to the former till the whole exhibits a rather deep greenish-blue colour.

Chrome ink.—**Runge** first suggested the preparation of ink with logwood and chromate of potassium. Such ink is more easily diluted than ordinary copperas-ink, and is not liable to turn mouldy; but on the other hand, it soon becomes viscid and gelatinous. Runge prepares it by mixing 16 pts. by weight of solid commercial extract of logwood, with 1,000 pts. water (or a decoction of 1 pt. of logwood boiled down to 8 pts. of liquid), and adds 1 pt. of yellow chromate of potassium dissolved in water. Göbel takes 24 pts. of solid logwood extract, 1,000 pts. water, and 2 pts. yellow chromate.

Vanadium ink.—Prepared by mixing a decoction of galls with vanadate of ammonia. It is black, and flows easily, because it does not contain any precipitate; it is not attacked by dilute alkalis, but acids turn it blue. (Berzelius.)

The *black-violet Rouen ink* (*encre bleue rouenaise*) is prepared by boiling 750 pts. of logwood with 6,000 pts. water, 35 pts. alum, 31 pts. gum-arabic, and 15 pts. sugar-candy, leaving the mixture to stand for two or three days, and straining through a linen cloth.

Ink in cakes.—42 pts. of good nut-galls and 3 pts. of madder are boiled in about six times their weight of water; the filtered decoction is mixed with 5¼ pts. copperas, and 2 pts. pyrolignate of iron; 1¼ pts. solution of indigo (in sulphuric acid, diluted with water) is then added; the mixture is evaporated nearly to dryness at a gentle heat, and with constant stirring; and the pasty mass is then made into cakes, and thoroughly dried. This ink dissolved in 6 pts. of hot water is said to make an excellent copying ink, and in 10 or 12 pts. water, a very fine writing ink.

Ink-powder.—A solid chrome-ink may be made by triturating together to a fine powder, 100 extract of logwood, 1 pt. neutral chromate of potassium, and $\frac{1}{10}$ indigo-carmine. 1 pt. of this powder added to 32 pts. water is said to make very good ink. A mixture of 4 pts. pounded galls, 2 pts. copperas, and 1 pt. gum-arabic is also frequently sold as an ink-powder.

Copying inks.—Inks for this purpose must be rather thick, not dry too quickly, and soften when moistened again, without becoming too fluid. The following preparation is much recommended: 4 pts. by weight of logwood-extract are dissolved in a mixture of 60 pts. vinegar, and 70 pts. water, and 3 pts. copperas, 2 pts. alum, 2 pts. gum-arabic, and 4 pts. sugar are then added. This ink is at first more violet than the Rouen ink, which is also used as a copying ink.

Indelible inks.—As writing executed with ordinary ink is liable to fade in course of time, the tannate and gallate of iron being gradually decomposed, and as, moreover, it is easily effaced by the action of certain chemical reagents (oxalic acid, hydrochloric acid, chlorine), it is desirable that valuable documents should be written with an ink not liable to destruction from such agencies. Various compositions have been proposed for this purpose. Most of them consist of common ink, or some other dark-coloured liquid in which finely divided carbon (Indian ink or lamp-black) is suspended. The simplest of all is made by mixing common ink with Indian ink (p. 246) rubbed up with weak hydrochloric acid. Writing executed with such ink cannot be bleached by chlorine or destroyed by acids; but the carbon may be ultimately removed by water, even when it is as finely divided as in Indian ink, and consequently penetrates the pores of the paper to a certain extent. Ink prepared in like manner with lamp-black is easily washed away. Traill's indelible ink is prepared by steeping wheat-gluten in water for 24 to 36 hours, then dissolving it with aid of heat, in strong vinegar, of specific gravity 1·033, or in pyroligneous acid, and then rubbing it up with Indian ink or lamp-black. This ink is of a fine black colour, and cannot be obliterated by water, chlorine, or dilute acids. Kind dissolves 1 pt. honey in 14 pts. water, adds 2 pts. strong sulphuric acid, and then adds a quantity of indigo-solution sufficient to render the ink visible in writing. A hot iron is then passed over the writing, whereby not only the honey is carbonised, but likewise a portion of the paper-fibre, by the action of the free sulphuric acid. The writing cannot be effaced by any chemical reagent, and only with great difficulty by mechanical means, since the ink penetrates deeply into the paper, and the charcoal is consequently separated within the pores; the paper is, however, very much attacked.

The vanadium-ink, above described, may also be used as an indelible ink; acids merely turn it blue; chlorine destroys the black colour, but does not efface the writing, even after long washing.

Red Ink.—Red ink is usually prepared either with cochineal or with Brazil-wood. The *cochineal inks* are the brightest, but at the same time the dearest and most fugitive. The best is a solution of pure carmine in caustic ammonia; it must be preserved in well-stopped vessels. Böttger recommends 1 pt. of good carmine, 120 caustic ammonia, and 1½ pt. gum-arabic. A cheaper but less brightly coloured ink is made by drenching 12 pts. of pulverised cochineal and 4 pts. of carbonate of ammonia (or pearl-ash) with 32 pts. hot water, then digesting and pouring off the clear liquid. Addition of cream of tartar and stannic chloride renders the ink more scarlet; cream of tartar and an equal weight of alum give it a crimson tint.

Brazil-wood inks are made by boiling the wood in water, adding tin-salt (stannous chloride) or cream of tartar and alum to modify the tint, and thickening with gum-arabic; *e.g.* 4 pts. Brazil-wood boiled in 60 pts. water, the decoction boiled down to 36 pts., filtered, and mixed with ⅛ pt. of tin-salt and ¼ pt. gum-arabic; or 8 pts. Brazil-wood, boiled with 2 pts. alum and 2 pts. cream of tartar in 120 pts. water; the liquid concentrated to 6 pts. by weight, and mixed with 2 pts. gum-arabic and 2 pts. sugar.

Blue inks.—The best is made by dissolving 30 pts. pure Prussian blue (Paris blue, ii. 227) in a solution of 4 pts. oxalic acid in 1,000 pts. water. A blue ink may also be prepared by dissolving 4 pts. of indigo-carmine in 64 pts. water, and mixing it with 1 pt. gum arabic; but it cannot be used with steel pens.

Yellow and green inks are sometimes, though very rarely, used. The former may be made with decoction of saffron or yellow berries; the latter of solution of verdigris mixed with turmeric or gamboge; or better of indigo-carmine mixed with picric acid. It may also be prepared from the green modification of chrome-alum, namely, by dissolving 3 pts. acid chromate of potassium in 8 pts. water, adding 1 pt. alcohol, then sulphuric acid by drops, and heating till the liquid assumes a brownish green colour; then diluting with 16 pts. water, adding a few more drops of sulphuric acid, leaving the liquid to stand, and adding a small quantity of gum-arabic.

Sympathetic inks.—This name is applied to inks which make characters invisible till brought out by heat or the application of some reagent. If a weak infusion of *galls* be used, the writing will be invisible till the paper is moistened with a weak solution of sulphate of iron. Dilute solutions of *gold* and *silver* remain colourless upon the paper till exposed to the sun's light, which gives a dark colour to the oxides, and renders them visible. Most *acids*, or *saline solutions*, diluted, and used to write with, become visible by heating before the fire, which concentrates them, and assists their action on the paper. Dilute *prussiate of potash* affords blue letters when wetted with solution of sulphate of iron. The solution of *cobalt* in aqua-regia, when diluted, affords an ink which becomes green when held to the fire, but disappears again when suffered to cool. This ink has been used in fanciful drawings of trees, the green leaves of which appear when warm, and vanish again on cooling. If the heat be continued too long after the letters appear, it renders them permanent. If oxide of cobalt be dissolved in acetic acid, and a little nitre added, the solution will exhibit a pale rose colour when heated, which disappears on cooling. A solution of equal parts of sulphate of copper and sal-ammoniac gives a yellow colour when heated, that disappears when cold.

Sympathetic inks have been proposed as the instruments of secret correspondence, but they are of little use in this respect, because their properties change by remaining on the paper for a few days; most of them have more or less of a tinge when thoroughly dry, and none of them resist the test of heating the paper till it begins to be scorched.

Marking inks.—Inks for marking linen must be able to withstand the action of water, soap, alkaline leys and acid liquids. The best are those which contain silver. They consist of a solution of nitrate of silver, usually coloured with sap-green, or other colouring matter, sometimes with lamp-black, and thickened with gum. It is best to prepare the part of the linen to be marked with a solution of carbonate of soda and gum, then smooth it with a hot iron, and after writing upon it, expose it to sunshine. The writing may be effaced by a solution of cyanide of potassium, with or without iodine.

Roder (Polyt. Notizblatt, 1856, p. 112) prepares a marking ink by dissolving 5 pts. molybdic oxide in hydrochloric acid, adding 240 pts. water, 6 pts, gum-arabic, and 2 pts. liquorice-juice. The writing is to be dried and then moistened with solution of stannous chloride. Inks containing gold or platinum have also been recommended for this purpose, but they are too costly for general use.

An ink for writing on *zinc plant-labels* may be made by dissolving equal parts acetate of copper and sal-ammoniac in distilled water. When characters are written with this solution on a zinc plate, the copper is precipitated, forming deep black, very durable marks.

Ink for marking *copper* and *silver* vessels may be made by boiling sulphide of antimony in strong potash-ley, leaving the liquid to cool, and filtering from separated kermes. As this liquid does not act upon iron, steel pens may be used for writing with it on the metal. The characters on copper and silver are black and very durable; on tin, lead, and zinc, less durable.

Printing ink.—All inks or paints used for letter-press, copper-plate, lithographic printing, &c. consist essentially of well-boiled drying oils (varnishes) mixed with lamp-black, or other pigment, according to the colour intended to be produced. Soap and resinous matters are sometimes added to give the boiled oil the required consistence.

The oil most frequently used for the preparation of the varnish is linseed oil; nut-oil is also used in localities where it can be had cheap; but it loses more weight in boiling than linseed oil, and does not easily acquire so firm a consistence. The oil should be old and well cleared, by deposition, from particles of mucus.

Ten or twelve gallons of the oil are set over the fire in an iron pot, capable of holding at least half as much more; for the oil swells up greatly, and its boiling over into the fire would be very dangerous. When it boils, it is continually stirred with an iron ladle; and if it do not itself take fire, it is kindled with a piece of flaming paper or wood: for simple boiling, without the actual inflammation of the oil, does not communicate a sufficient degree of the drying quality required. The oil is suffered to burn for half an hour or more, and the flame being then extinguished by covering the vessel close, the boiling is afterwards continued with a gentle heat, till the oil appears of a proper consistence; in this state it is called varnish.[*] It is necessary to have two kinds of this varnish, a thicker and a thinner, from the greater or less boiling, to be occasionally mixed together as different purposes may require, that which answers well in hot weather being too thick in cold, and large characters not requiring so stiff an ink as small ones.

The thickest varnish, when cold, may be drawn into threads like weak glue, by which criterion the workmen judge of the due boiling, small quantities being from time to time taken out and dropped upon a tile for this purpose. It is very viscid and tenacious, like the soft resinous juices, or thick turpentine. Neither water nor alcohol dissolves it; but it mingles readily enough with fresh oil, and unites with mucilages into a mass diffusible in water in an emulsive form. The oil loses from one-tenth to one-eighth of its weight by boiling into the thick varnish.

For letter-press printing ink, the addition of soap to the varnish is indispensable, to enable the ink to be taken up clearly from the types by the moistened paper, without smearing. The soap used for the purpose is yellow resin-soap; it is cut into thin slices, well dried, rubbed to coarse powder, and incorporated by small portions at a time with the varnish, which is then once more placed over the fire, to expel any remaining moisture.

The colouring matter of black printing ink is the best lamp-black, previously calcined to free it from empyreumatic oils and resins. Its somewhat brownish colour is corrected by the addition of a little Prussian blue or indigo.

The ink used by copper-plate printers differs in the oil, which is not so much boiled as to acquire the adhesive quality. This would render it less disposed to enter the cavities of the engraving, and more difficult either to be spread or wiped off (Ure).[†] The black is likewise of a different kind. Instead of lamp-black, or sublimed charcoal, the Frankfort black is used, which is a residual or denser charcoal, said to be made from vine-twigs. Lamp-black is said to give a degree of toughness to the ink, which the Frankfort does not; but the goodness of the colour seems to be the leading inducement for the use of the latter.

For red, blue, and yellow printing inks, the ordinary linseed oil varnish is not very well adapted, as its brown colour impairs the brightness of the tint. A good varnish for the purpose may be made by mixing copaïba balsam (previously subjected to rapid boiling with water for several hours in an open dish, to render it more tenacious, and diminish the unpleasant odour) with $\frac{1}{20}$ to $\frac{1}{10}$ of its weight of pulverised white curd soap, then warm the mixture a little, and incorporate it with the pigment previously rubbed to fine powder with spirit of wine, and dried. For the lighter colours, it is best to mix very deep-coloured pigments with a considerable quantity of carbonate of magnesia. In that case, light-coloured linseed-oil varnish mixed with $\frac{1}{20}$ white soap may be used. A fine red is formed of vermillion mixed with $\frac{1}{10}$ carmine, and $\frac{1}{8}$ magnesia. Blue is given by ultramarine (the darkest varieties used in calico-printing) with magnesia; yellow by chromate of lead. Prussian blue mixed with chrome-yellow and a large quantity of magnesia, or ultramarine with chromate of zinc, yields a fine green. Browns are obtained with bistre and sepia.

Lithographic printing ink is made in the same way as common printing ink, but with a larger proportion of lamp-black, and without addition of soap. (See LITHOGRAPHY.)

For further details on printing inks, see *Handwörterbuch der Chemie*, vii. 388, and *Ure's Dictionary of Arts*, &c. iii. 530.

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[*] The description of the process given in the text is taken from *Ure's Dictionary of Chemistry* (3rd ed. 1831). Mr. Savage also, in his work on the *Preparation of Printing Ink* (London, 1832) says that good varnish for printing ink cannot be made without allowing the oil to burn. The German practice appears, however, to be somewhat different; for in the *Handwörterbuch der Chemie* (Bd. vii. p. 391) it is stated that the oil should be heated only till the vapour which rises from it can be set on fire with a piece of burning paper, but will cease to burn of itself after a little while, or at least will be easily extinguished by putting on the cover; further, that if this temperature be exceeded, there is great danger of the oil getting into a state of violent combustion, which cannot be extinguished even by covering the vessel, and may occasion an enormous loss of oil.

[†] In the *Handwörterbuch der Chemie* (vii. 399) it is stated, on the contrary, that ink for copper-plate printing is prepared with the thickest linseed-oil varnish, which has been allowed to burn.

INOCARPIN. A red colouring matter contained in the juice of *Inocarpus edulis*, a tree growing in Tahiti. The juice which exudes from incisions in the bark of young trees, or the pericarp of green fruits, is colourless, but soon turns red on exposure to the air (the juice of old trees is red as soon as it runs out), and dries up to a red gummy mass, soluble in water and in alcohol, insoluble in ether. The aqueous solution mixed with caustic alkalis exhibits a peculiar play of colours when shaken up with air. The reddened juice contains also a yellow colouring matter called xanthocarpin. (Cuzent, J. Pharm. xxxv. 241.)

INOSIC ACID. $C^5H^8N^2O^6$ (?) (Liebig, Ann. Ch. Pharm. [3] xxxiii. 129.)—An acid found in the mother-liquor of the preparation of creatine from flesh-juice. When this mother-liquor is concentrated, then mixed with alcohol till it acquires a milky consistence, and left to itself for a few days, it deposits a crystalline mixture consisting of creatine, inosate of potassium, inosate of barium, and various substances of unknown composition. The crystals are redissolved in hot water, and chloride of barium is passed into the solution, which then, on cooling, deposits crystals of inosate of barium; and this salt, decomposed by sulphuric acid, yields inosic acid.

Inosic acid is uncrystallisable, easily soluble in water, and has a very agreeable flavour of broth. Alcohol precipitates it from its aqueous solution. It is insoluble in ether. It does not precipitate barium- or calcium-salts, but with copper-salts it forms a bluish-green precipitate, insoluble in boiling water. With lead-salts it forms a white precipitate; and with silver-salts, a white gelatinous precipitate, having the aspect of alumina, soluble in nitric acid and in ammonia.

Inosic acid, heated with peroxide of lead and a small quantity of sulphuric acid, is decomposed, and the filtered liquid contains needle-shaped crystals. The *inosates*, heated on platinum-foil, decompose, giving off an odour of roast meat.

Inosate of potassium forms elongated quadrilateral prisms, very soluble in water, insoluble in alcohol. It gives off 22·02 per cent. of water at 100°, and the dried salt contains 20·7 per cent. potash. The *sodium-salt* crystallises in small silky needles, very soluble in water; insoluble in alcohol. The *barium-salt* forms elongated quadrilateral scales, having a nacreous lustre. 3,000 pts. of water at 16° dissolve 2·5 pts. of this salt; it is insoluble in alcohol. A solution, saturated at 70°, deposits part of the salt when raised to the boiling heat. The crystals, dried at 100°, contain 24·5 to 24·8 per cent. C, 2·6 H, 11·4 N, 31·1 to 33·8 O, and 30·4 Ba^2O; whence Liebig deduces the formula $C^5H^6Ba^2N^2O^6.\frac{7}{2}H^2O$. Gerhardt considers the composition to be more correctly represented by the formula $C^5H^7BaN^2O^6.3H^2O$. The crystals effloresce in the air, giving off 19·07 per cent. water,

Inosate of copper is nearly insoluble in water and in acetic acid; very soluble in ammonia. *Inosate of silver* is sparingly soluble in pure water, and does not blacken by exposure to light.

INOSITE. $C^6H^{12}O^6$. *Inosin. Phaseomannite.* (Scherer [1850], Ann. Ch. Pharm. lxiii. 322; lxxxi. 375.—Vohl, *ibid.* xcix. 125; ci. 50.—Cloetta, *ibid.* xcix. 289.—W. Marmé, *ibid.* cxxix. 222.)—A saccharine substance isomeric with glucose, discovered by Scherer in the muscular substance of the heart (hence its name, from ἴς, *ἰνός*, muscle), and since found to exist in the lungs, kidneys, liver and spleen of oxen (Cloetta), also in the brain (W. Müller); in the human kidneys and in the urine, in a case of Bright's disease: at most to the amount of 0·1 per cent. It occurs also in several plants, having been obtained from green kidney beans, the unripe fruit of *Phaseolus vulgaris* (Vohl); from the green pods and unripe seeds of the garden pea (*Pisum sativum*); the unripe fruit of the lentil (*Ervum lens*), and of the common acacia (*Robinia pseudacacia*); from the heads of the common cabbage (*Brassica oleracea*, var. *capitata*); from the herb of foxglove and from extract of digitalis; from the leaves and stems of dandelion (*Taraxacum dens leonis*), not from the flowers or roots; from the shoots of the potato; from the green herb and unripe berries of asparagus; and from two cryptogamous plants, *viz. Lactarius piperatus*, L., and *Clavaria crocea*, Pers. (Marmé.)

Preparation.—From organs of the animal body. 1. The muscle of the heart, or other organs containing inosite, is exhausted with water, as for the preparation of creatine; the phosphates are precipitated from the liquid by baryta-water; the filtrate is evaporated; and the creatine allowed to crystallise out. The mother-liquor is treated with dilute sulphuric acid to remove the dissolved baryta, and, after removal of the sulphate of barium, heated as long as volatile acids escape. It is then, in order to remove the last traces of volatile acids and of lactic acid, repeatedly shaken up with ether as long as anything is dissolved. The liquid, separated from the ether, is mixed with alcohol till a turbidity begins to appear; then, after standing for some time, it is poured off from the precipitated sulphate of potassium, and mixed with more alcohol, whereby crystals of inosite mixed with sulphate of potassium are obtained. The crystals of the former are picked out and dissolved in a small quantity of warm water, which leaves the more difficultly soluble sulphate of potassium, and are purified by recrystallisation (Scherer).—2. The fresh-chopped tissue is covered with water, and allowed to stand for 24 hours in a cool place, with frequent stirring; the liquid is then separated, and the residue pressed; the solution is heated with a little acetic acid to separate albumin and hæmatin, then strained, evaporated on the water-bath to one tenth, precipitated with neutral acetate of lead, and filtered; and the filtrate is mixed with basic acetate of lead, whereupon inosite is thrown down in combination with oxide of lead, accompanied by uric acid, cystine, and other substances. The precipitate, after washing, is decomposed under water by sulphydric acid, and the liquid filtered from the sulphide of lead; it then sometimes deposits crystals of uric acid, and when evaporated to a small bulk on the water-bath, and mixed with alcohol till a turbidity is produced, it yields crystals of inosite (Cloetta). Acetate of lead may also be added at once to the water used for making the extract (W. Müller).—3. The liquid from which the inosite is to be separated is concentrated by evaporation, and mixed, boiling, with three or four measures of alcohol; if a large precipitate, which sticks to the bottom, is thus produced, the liquid is poured off hot; but if only a slight, not sticky precipitate is produced, the hot solution is filtered through a previously heated funnel, and left to stand for 24 hours; crystals of inosite are then deposited, and are washed with a small quantity of cold alcohol. If the precipitate caused by hot alcohol is dissolved in a small quantity of boiling water, and treated like the first solution, a further quantity of inosite is obtained. In case no inosite separates from the cooled solution, the crystallisation may be facilitated by addition of ether until a turbidity remains after shaking. (Cooper Lane, Ann. Ch. Pharm. cxvii. 118.)

From kidney beans and other vegetable organs.—The fruit cut up in the bean-mill is hung in a pressing bag for half an hour in boiling water, or in steam, whereby it becomes possible to press it; the expressed liquid is then evaporated to a syrup on a water-bath, and alcohol is added till a permanent turbidity is produced. The crystals which form are purified by repeated crystallisation from water, with help of animal charcoal. (Vohl.)

Marmé, after freeing the aqueous extracts of the plants above mentioned from everything precipitable by tannic acid and neutral acetate of lead, and decolorising them as completely as possible with milk of lime or animal charcoal, precipitated them with basic acetate of lead; mixed the filtrate with ammonia, whereby a second precipitate was obtained; decomposed both precipitates with sulphydric acid; concentrated the filtrate on the water-bath till it became turbid on addition of alcohol; then mixed it with a double volume of alcohol; warmed the liquid till it became clear; and left it to itself for several days, adding a little ether if necessary, as in Cooper Lane's method. The sulphide of lead sometimes obstinately retains small quantities of inosite, which can only be removed by boiling with water.

Properties.—Inosite is deposited from its concentrated aqueous solution in crystals containing 2 at. water, $C^6H^{12}O^6.2H^2O$. According to Vohl, the crystals are tabular, like those of gypsum; according to Scherer, they are oblique prisms, arranged for the most part in groups like cauliflower-heads; according to Cloetta, they are right rhombic prisms with angles of 138·52° and 41·8°. Specific gravity = 1·1154 at 5° (Vohl). In dry air, in vacuo over sulphuric acid, or at 100°, they become white and opaque, and give off their water, leaving anhydrous inosite, $C^6H^{12}O^6$, as a white effloresced mass, which melts at a temperature above 210°, yielding a colourless liquid, which solidifies in the crystalline state when quickly cooled, and to an amorphous mass when cooled slowly, but does not lose weight or undergo further alteration (Scherer). Anhydrous inosite separates in white, opaque crystals from the aqueous solution cooled below 0°. (Vohl). Inosite has a pure sweet taste and no rotatory power.

Hydrated inosite dissolves in 6 pts. *water* at 19° (Vohl), in 6½ pts. at 24° (Cloetta). The concentrated solution, of specific gravity 1·0548 at 19°, is not syrupy and not subject to spontaneous decomposition. Inosite is slightly soluble in cold aqueous *alcohol*, more soluble at the boiling heat; insoluble in absolute alcohol and in *ether*.

Inosite does not combine with *chloride of sodium* or *chloride of potassium*, these salts crystallising out unaltered from its aqueous solution. The aqueous solution forms, with *basic acetate of lead*, a precipitate which appears to contain $C^6H^{12}O^6.2Pb^2O$.

Decompositions.—1. After dehydrated inosite has been melted above 210°, it swells up when more strongly *heated*, and evolves gas which burns with a pale blue flame; it is afterwards charred, and then burns with a brightly luminous flame, leaving an easily combustible cinder (Scherer). When quickly heated, it gives off vapours which excite tears and produces a smell of burnt sugar (Vohl).—2. Aqueous inosite is not affected by *ozone* (Gorup-Besanez, Ann. Ch. Pharm. cx. 103).—3. The solution of inosite in dilute *nitric acid* does not give off nitrous acid till moderately concentrated; after evaporation to dryness, it contains oxalic acid. The aqueous solution of the residue, freed from oxalic acid by carbonate of calcium, deposits on standing magnificent purple-red flocks, soluble in dilute acids and precipitable without alteration by ammonia (Vohl). When aqueous inosite is evaporated nearly to dryness with nitric acid, and the residue is moistened with ammonia and a small quantity of solution of chloride of calcium, and again evaporated, a rose-red substance remains. This reaction affords a delicate and characteristic test of the presence of inosite (Scherer, Vohl). Inosite dissolves without evolution of gas, in cold or boiling nitric acid of specific gravity 1·52, forming a solution whence oil of vitriol precipitates nitro-inosite (Vohl).—4. Inosite dissolves without coloration in *sulphuric acid*, either cold or at 100°; is not blackened till more strongly heated, and then evolves sulphurous anhydride (Vohl). It is not altered by boiling with dilute *acids* (Scherer, Vohl).—5. It may be boiled with concentrated *potash-ley*, or with *baryta-water*, without alteration or coloration (Scherer, Vohl).—6. The aqueous solution mixed with *cupric sulphate*, yields, on addition of potash-ley, a bluish green precipitate which quickly disappears on addition of excess of potash. No cuprous oxide separates from the solution in boiling, but a light blue precipitate falls when the liquid is left to stand for several days (Scherer). Aqueous inosite yields, when heated with *potassio-cupric tartrate*, a green solution, whence a bulky green precipitate separates, the supernatant liquid again becoming blue. After removing the precipitate, the filtrate shows the same change of colour when heated (Cloetta). According to Vohl, the change of colour which occurs on heating the deep azure-blue mixture of inosite and potassio-cupric tartrate, is not very striking, and is due, as well as the production of the precipitate, to the presence of traces of foreign substances.—7. Inosite is not capable of undergoing vinous fermentation (Scherer). In contact with *cheese*, *flesh*, or decaying *membrane*, and chalk, it undergoes lactous fermentation, carbonic, lactic, and butyric acids being formed. (Scherer, Vohl.)

Nitro-inosite. $C^6H^6N^6O^{18} = C^6H^6(NO^2)^6O^6$. *Inosine hexnitrique.* (Vohl, *loc. cit.*)—This compound is obtained by dissolving anhydrous inosite in nitric acid of specific gravity 1·52, and precipitating the solution with sulphuric acid. The product, which, according to the temperature attained by the mixture, separates either as a powder or as oil-drops which solidify to crystalline masses, is well washed with water and recrystallised from boiling alcohol. It forms rhombohedrons, often some lines in length; melts to an oil when heated, and solidifies to an amorphous mass which becomes crystalline after a few days. It is permanent in air, either dry or moist; insoluble in *water*, easily soluble in *alcohol*.

Nitro-inosite deflagrates without residue when quickly *heated*, and detonates under the hammer. It is decomposed when warmed with concentrated acids. It dissolves, with dark brown colour and evolution of ammonia, in cold or warm *potash-ley*. The alkaline solution precipitates cuprous oxide from *potassio-cupric tartrate*, and a mirror of metallic silver from *ammonio-nitrate of silver*. Nitro-inosite treated with *nitric acid*, *ammonia* and *chloride of calcium*, shows the coloration of inosite.

INSOLINIC ACID. See TEREPHTHALIC ACID.

INTESTINAL CONCRETIONS. These concretions are of rare occurrence in man and in carnivorous animals, but occur more frequently in herbivorous animals, especially in horses. They exhibit great diversity in their properties and composition, as well as in their origin. Many owe their origin to an albuminous exudate or blood-coagulum, which is retained in the intestine, and gradually solidified by resorption of the soluble portion. These stones consist mainly of coagulated fibrin mixed with calcium-salts and remains of food, and sometimes containing a foreign body as nucleus. In a concretion of this kind from the intestine of a child, Davy found 74 per cent. fibrin, 19 per cent. of other organic matters, and 7 per cent. inorganic salts.

A second kind of intestinal concretion consists chiefly of earthy salts, calcic phosphate and carbonate, ammonio-magnesic carbonate, and magnesic carbonate mixed or unmixed with remains of food; such stones often contain a foreign nucleus. They are most frequent in vegetable feeders, especially in horses, and often attain a weight of several pounds. A concretion from the cœcum of a cart-horse, analysed by F. Simon, was spherical, perfectly smooth, greyish-yellow, weighed 12½ oz., and consisted of three layers, deposited round a fragment of granite. All three layers consisted of ammonio-magnesian phosphate, with a small quantity of alkaline phosphates, but no phosphate of calcium. The middle layer exhibited a radiating structure from the centre outwards, with woody fibres interposed in like manner amongst the stony mass. In 100 pts., Simon found 81·11 ammonio-magnesian phosphate, and 1·5 per cent. alkaline phosphates.

Children examined stones from the colon of a man, which weighed from 500 to 1,000 grms., and consisted of plum-stones, surrounded by a smooth compact mass made up of alternate layers of earthy phosphates and ligneous matter.

The formation of these stones is due to the precipitation of earthy salts originally dissolved in the food, and their subsequent agglomeration by intestinal mucus, or round a foreign body.

A third kind of intestinal concretion consists chiefly of undigested residues of food; such stones have usually a woody consistence, and are formed round a foreign body. Laugier examined a concretion of this kind from the rectum of a man; it consisted of a nucleus of bone, surrounded by interlaced vegetable fibres, from which water extracted 14 per cent. of animal matter having a fæcal odour, together with small quantities of sal ammoniac and chloride of calcium.

Another class of intestinal concretions consists of fatty matters mixed with small quantities of fibrin and calcium-salts. Lassaigne analysed a number of small concretions of this kind voided by a girl suffering from tuberculosis. They contained 74 per cent. fatty matters (for the most part free fatty acids, perhaps oleic and stearic), 21 animal matter, 4 phosphate of calcium, and 1 chloride of sodium.

Bezoar-stones (i. 584) must also be classed amongst intestinal concretions. (Handwörterbuch d. Chem. 2te Aufl. ii. [3] 374.)

INTESTINAL JUICE. The mucous secretion of the pouch-like glands of the intestinal canal (the Lieberkühnian glands of the small intestine and the follicles of the colon). When viewed by the microscope, it exhibits granulated cells and cell-nuclei, and, as commonly obtained, likewise small quantities of fat and epithelium. When filtered from these matters, it forms a tolerably clear, mucous, strongly alkaline liquid, which does not coagulate by heat, and is not precipitated by acetic acid, nor, when mixed with that acid, by chloride of barium. When mixed, however, with eight or ten times its volume of alcohol, it deposits white flocks, which dissolve easily and completely in water; the solution thus obtained is not precipitated by hydrochloric, sulphuric, or acetic acid, or by mercuric chloride, but gives precipitates with the neutral and basic acetates of lead.

The constituents of pure intestinal juice are the same as those of mucus. In 1,000 pts. of the filtered intestinal juice of a dog, Schmidt and Zander found 965·3 water, 34·7 solid matter, 9·6 punceratic and intestinal ferments, together with insoluble salts, 16·6 biliary matters (cholic, taurocholic, and glycocholate of sodium), 6·3 taurine, 0·7 fat, 3·7 extractive matter, 0·15 potassium, 1·45 sodium, 2·11 chlorine, 0·03 phosphoric anhydride, 0·06 earthy phosphates. In the intestinal juice from the upper part of the colon of a man, Busch found from 3·8 to 7·4 per cent.; Frerichs, from 2·2 to 5·6 per cent. solid matter.

The intestinal juice converts starch very quickly into sugar, and digests albuminous substances, flesh, &c., though much more slowly than the gastric juice. (Handwörterbuch d. Chem. 2te Aufl. ii. [3] 373.)

INULIN. $C^6H^{10}O^5$. *Helenin, Alantin, Menyanthin, Dahlin, Synantherin, Sinistrin.*—A substance isomeric with, and similar in its properties to, starch, discovered by Valentin Rose in 1804. It appears to be a very widely distributed constituent of plants, and is found especially in the roots of elecampane (*Inula Helenium*), dandelion (*Taraxacum dens leonis*), chicory (*Cichorium Intybus*), feverfew (*Pyrethrum Parthenium*), and meadow saffron (*Colchicum autumnale*); in the tubers of the potato, the dahlia, and the Jerusalem artichoke (*Helianthus tuberosus*), in Lerp-manna (from *Eucalyptus dumosa*), and probably in the seeds of the sun-flower (*Helianthus annuus*), and in certain lichens, viz. *Lichen fraxineus* and *Lichen fastigiatus.*

Preparation.—a. From Elecampane-roots.—The roots are boiled with a large quantity of water, the decoction is evaporated, the extract exhausted with cold water, and the inulin which remains undissolved is washed (Gaultier, Stratingh).—Or the roots are exhausted with hot water in a percolating apparatus; the concentrated effusion is evaporated to 10° or 12° Bm. and mixed with 2 pts. alcohol; and the inulin thereby precipitated is purified by reprecipitation with alcohol from its concentrated solution, and decolorised with animal charcoal (Thibault).—The helenin mixed with inulin prepared from elecampane-roots is extracted by boiling with alcohol. (Croockwit.)

b. From Potatoes or Dahlia-tubers.—1. The pulverulent deposit which separates in the cold from the expressed juice of potatoes is dissolved in hot water, and the solution is filtered, evaporated, and left to cool, whereupon it deposits inulin (Braconnot).—2. The nearly transparent juice expressed from dahlia-tubers is left to stand for some hours, whereupon it solidifies, from separation of inulin, to a stiff paste, which is to be washed and dried (Ludwig, N. Br. Arch. 82, 163).—3. Dahlia-tubers rubbed to a pulp are washed on a hair-sieve in a thin stream of water, as long as the liquid continues to run through milky, and the inulin which separates from it on standing is collected; or in case it is slow in settling down, the turbid liquid is heated till it boils, the coagulated vegetable albumin is skimmed off, and the remaining liquid is left to cool; it then, after a few days, deposits a thick pulp easy to wash (Liebig, Ann.

Pharm. 2, 235).—4. Dahlia-tubers rubbed to a pulp are washed with cold water on a linen or woollen cloth; the residue is boiled for half-an-hour with 2 pts. water and a small quantity of chalk; the liquid is expressed; the extract, after being decolorised with animal charcoal and clarified with albumin, is evaporated till a film forms on it; and the inulin which separates on cooling is washed with cold water, and purified by solution in hot water and cooling. (Payen.)

Parnell uses peeled and washed dahlia-tubers, boils them for an hour and a half with 5 pts. of water, and purifies the inulin which separates from the evaporated extract by precipitating its aqueous solution with alcohol. Croockwit purifies the inulin thus obtained by boiling it with alcohol.

c. From Dandelion-roots. Obtained in the same way as from dahlia-tubers. (Wittstein, Repert. 71, 362; Herberger, Repert. 52, 399).

d. From Chicory-roots. The aqueous decoction is precipitated by neutral acetate of lead; the filtrate freed from lead is evaporated till a film forms on the surface; and the inulin which separates from it is purified by precipitating its aqueous solution with alcohol. (Woskresensky.)

e. From Lerp-manna. The substance is exhausted with boiling alcohol; the residue, consisting of starch, cellulose and inulin, is well boiled with water, and the inulin, which separates from the filtered extract on cooling, is collected and washed till the wash-water no longer exhibits the reactions of starch. (Anderson.)

Properties.—Inulin is a soft, white, tasteless, inodorous powder, resembling starch. When dried on glass or porcelain, it forms a translucent, brittle, dazzling white mass, which swells up in water. Specific gravity = 1·356 (Payen), 1·462 (Dubrunfaut). It is very hygroscopic, and sticks to the teeth and to moist paper. It exhibits lævo-rotatory power = 34° 42′. (Dubrunfaut, Compt. rend. xlii. 803.)

Most of the analyses which have been made of inulin agree nearly with the formula $C^6H^{10}O^5$. Woskresensky, however (J. pr. Chem. xxxvii. 309) obtained quantities of carbon and hydrogen much too large for this formula: he accordingly represents inulin by the formula $C^{24}H^{19}O^{14}$ (or $C^{24}H^{38}O^{14}$), and supposes that the inulin analysed by other chemists must have undergone partial oxidation; but the near accordance of most of these analyses renders this view improbable.

		Calculation.		Payen, at 150°. *a.*	Payen, at 170°. *b.*	Mulder, at 120°. *c.*	Mulder, at 120°. *d.*	Parnell, air-dried. *e.*
6	C	72	44·44	44·55	44·19	44·13	43·8	43·37
10	H	10	6·17	6·12	6·17	6·19	6·2	6·40
5	O	80	49·39	49·33	49·64	49·68	50·0	50·23
$C^6H^{10}O^5$		162	100·00	100·00	100·00	100·00	100·0	100·00

	Croockwit, at 120°—160°. *f.*	Croockwit, at 120°—160°. *g.*	Woskresensky, at 100°—120°. *h.*	Woskresensky, at 100°—120°. *i.*	Anderson, at 150°. *k.*	Dubrunfaut, at 100°. *l.*
C	43·37	43·48	52·18	49·59	44·03	44·32
H	6·23	6·25	6·86	6·86	6·30	6·19
O	50·49	50·27	40·96	43·55	49·67	49·49
	100·00	100·00	100·00	100·00	100.00	100·00

a, *b*, from Iceland moss; *c*, from dandelion-root; *d*, from elecampane-root; *e*, *f*, *g*, from dahlia-tubers; *h*, from chicory-roots; *i*, from dandelion-roots (partially oxidised); *k*, from lerp-manna.

Inulin, immersed in cold water, or exposed to moist air, absorbs water, and crumbles to a dull-looking powder, consisting of *hydrated inulin*, $C^{12}H^{20}O^{10}.3H^2O$.

Inulin dissolves very sparingly in cold *water*, freely in boiling water, but the solution does not form a jelly like that of starch; it is insoluble in *alcohol*, which also precipitates it from its aqueous solution. It dissolves with brown colour in strong *sulphuric acid*, and is precipitated therefrom by ammonia, but not by water or alcohol. It is insoluble in *hydrochloric acid*, and in cold glacial *acetic acid*, but dissolves in the latter when warmed. The aqueous solution is not precipitated by *chlorine-water*, but forms a white precipitate with *infusion of galls*.

Inulin absorbs 3 per cent. *ammonia*, and dissolves in cold aqueous *potash*, forming a solution which leaves on evaporation a nearly colourless gum, and when mixed with acids, deposits, after a while, unaltered inulin.

Inulin dissolves in aqueous *cuprammonia* (an ammoniacal solution of cupric oxide), without previous tumefaction (Cramer, J. pr. Chem. lxxiii. 16), the solution yielding after a few hours, a copious blue amorphous precipitate, insoluble in water and in ammonia, soluble in tartaric and nitric acids (Schlossberger, J. pr. Chem. lxxiii. 373). It dissolves gradually in aqueous *nickel-ammonia*. (Schlossberger.)

The aqueous solution of inulin forms a white precipitate with *baryta-water*, and with chloride of barium mixed with potash.

It does not precipitate aqueous *acetate of lead*, either neutral or basic, but with a solution of the neutral acetate containing ammonia, it forms a white precipitate containing quantities of lead-oxide varying in amount from 51·23 to 62·43 per cent. It is not precipitated by *ferrous*, *ferric*, or *cupric sulphate*, *mercuric nitrate*, *nitrate of silver*, or *chloride of gold*.

Decompositions.—1. Inulin heated above 100° melts, with colouring and loss of weight, and is converted into a pitchy, sweetish substance, very soluble in water (Braconnot), insoluble in water and in alcohol (Payen). By dry distillation it yields acetic acid, having a brown colour, but free from oily matter. When thrown on glowing coals, it emits the odour of burnt sugar.—2. Heated with *water* to 100°, it is slowly but completely converted into non-crystallisable, lævo-rotatory, fermentable sugar.—3. By boiling with *nitric acid*, inulin is converted into malic, oxalic, and acetic acids, but not into mucic acid. Its solution in fuming nitric acid is not precipitated by water.—4. When heated with strong *sulphuric acid*, it turns yellow, then brown, and is ultimately carbonised.—5. By *dilute acids*, either hot or cold, inulin is converted into sugar, without evolution or absorption of gas.—6. Aqueous *arsenic acid* dissolves inulin, with aid of heat; after continued action, the cooled solution no longer deposits inulin, but leaves, on evaporation, a rose-coloured mass, which afterwards becomes darker, and finally black, grape-sugar being first formed, afterwards formic and ulmic acids.—7. *Oxide of lead* converts inulin wholly or partially into glucic acid, which, if afterwards exposed to the air, is changed into apoglucic acid. A warm aqueous solution of inulin reduces other salts of lead, also those of copper and silver. When an ammoniacal solution of acetate of lead is precipitated by aqueous inulin, the filtrate separated from the white precipitate deposits spangles of lead after a few hours, and contains formic acid.—8. Inulin is not *fermentable*. Neither its rotatory power nor any of its other properties is altered by *diastase*.—9. It is digested in the stomach, and does not pass, as inulin, either into the urine or into the fæces.

Inulin is distinguished from starch by its reaction with *iodine*, which imparts to it only a fugitive brown colour; by its solubility in aqueous cuprammonia, by its power of reducing certain metals from their solutions; and by its inalterability under the influence of ferments.

IODACETIC ACID. $C^2H^3IO^2 = \left.\begin{matrix} C^2H^2IO \\ H \end{matrix}\right\}O$. (Perkin and Duppa, Phil. Mag. [4] xviii. 54.)—This acid is obtained, as an ethyl-compound, by the action of iodide of potassium on bromacetate of ethyl diluted with three measures of alcohol, the mixture being digested at 40° in the dark for about two hours, and the iodacetic ether then distilled off. To obtain the free acid, the ether is converted into a barium-salt by digestion with hydrate of barium; this salt is decomposed by cautious addition of sulphuric acid; and the filtrate is crystallised in a vacuum.

Iodacetic acid forms thin, tough, colourless, rhombohedral plates, having a very sour taste, and not deliquescent. It melts at 82°, with slight decomposition, and solidifies again at 85°. It is decomposed, like bromacetic acid, by moist oxide of silver, with formation of glycollic acid:

$$C^2H^3IO^2 + AgHO = AgI + C^2H^4O^3.$$

Iodacetate of Ammonium is very soluble, crystalline, and non-deliquescent. The *potassium*-salt exhibits similar properties. The *barium*-salt, $C^2H^2IBaO^2$, is crystalline, moderately soluble in water, and precipitated by alcohol. The *lead-salt* crystallises in prisms, but easily splits up in solution into iodide of lead and glycollic acid:

$$C^2H^2IPbO^2 + H^2O = PbI + C^2H^4O^3.$$

Iodacetate of Ethyl is an oily liquid, heavier than water, and having a very irritating odour. *Iodacetate of Amyl* is oily, heavier than water, has the odour of pears, and gives off an irritating vapour.

Di-iodacetic Acid. $C^2H^2I^2O^2$. (Perkin and Duppa, Chem. Soc. Qu. J. xiii. 1.)—The ethyl-compound of this acid, obtained by acting on dibromacetate of ethy with iodide of potassium, is converted into a calcium-salt by means of milk of lime; the calcium-salt is decomposed by hydrochloric acid, avoiding an excess; and the solution is left to crystallise. The acid is thus obtained as a beautifully crystalline sulphur-yellow compound, volatile at ordinary temperatures, and slightly soluble in water. It has a faintly acid taste, with metallic after-taste. It does not blister the skin.

The *di-iodacetates* are slightly yellow, crystalline, and permanent, excepting the potassium and sodium-salts, which are deliquescent. The *barium*-salt, $C^2HI^2BaO^2$, forms rhombohedral crystals, which give off iodine when heated. The *calcium*-salt forms yellow silky needles, also decomposed by heat. The *lead*-salt, $C^2H^2IPbO^2$, is obtained as a crystalline precipitate by adding a solution of the sodium-salt to acetate of lead, both being largely diluted. The *silver*-salt, prepared in like manner, forms a yellow crystalline powder, which, when gently heated, decomposes with slight explosion and evolution of iodine.

Di-iodacetate of Ethyl, $C^2H(C^2H^5)I^2O^2$, is a yellowish liquid, having a pungent, burning taste, and extremely irritating odour. It is insoluble. or nearly so, in water. Ammonia rapidly converts it into di-iodacetamide, $N.H^2.C^2HI^2O$, which is a pale yellow substance, sparingly soluble in water.

IODACETYL. C^2H^2IO.—The radicle of iodacetic acid.

IODAL. $C^2HI^3O = C^2I^3O.H$. *Hydride of Tri-iodacetyl* (i. 34).—This compound is said to be obtained by adding iodine to a mixture of alcohol and nitric acid. The iodine rapidly disappears, and an oil separates which may be purified by agitation with water and distillation over chloride of calcium. It begins to boil at 25°, but the boiling point gradually rises to 115°. Potash converts it into iodoform (Aimé, Ann. Ch. Phys. [2] lxiv. 217). Johnston (Phil. Mag. [3] ii. 215) obtained, by a similar process, an oily liquid which boiled at 110°, but decomposed and turned brown at the same time. Johnston regarded the product as iodate of ethyl (see Gmelin's Handbook, ix. 186). Schoonbroodt (Bull. Soc. Chim. de Paris, 1861, p. 109), by adding hypochlorite of potassium to an alcoholic solution of iodine till the latter was decolorised, obtained a copious precipitate consisting of small shining needles, easily soluble in water, sparingly in alcohol, and resolved by potash-ley into formic acid and iodoform: hence it was probably iodal.

IODAMIDES and **IODAMMONIUMS.** Under these terms may be included a number of compounds, mostly of an explosive character, produced by the action of iodine on ammonia. The composition and properties of these products vary according to the mode of preparation adopted.

I. **Iodamides.** By digesting iodine in excess of aqueous ammonia; by adding a large excess of aqueous or alcoholic ammonia to a saturated solution of iodine in alcohol, and then diluting with water; by adding ammonia to a solution of iodine in nitro-muriatic acid (which contains protochloride of iodine, ICl); or by decomposing the explosive compound called chloride of nitrogen, with iodide of potassium—a black powder is precipitated which when dry is violently explosive. It must be collected on a filter, and washed with water; and to guard against accidents in drying, it is advisable to divide the filter, with the moist precipitate upon it, into small pieces, and expose them to warm dry air at considerable distances from each other. Or the precipitate may be dried under a receiver filled with ammonia gas, in which case, according to Millon, there is no fear of explosion.

The product obtained by either of these processes, commonly called iodide of nitrogen, is a brownish-black soft powder, which when dry explodes from the slightest cause, producing a loud report and destroying any solid bodies that may be near it. The explosion is attended with a faint flash of violet light, nitrogen being set free as gas, and iodine in the form of very fine powder. It may be exploded by friction, even under water, and in the dry state can scarcely be touched without exploding, the slightest elevation of temperature, and even the friction produced by sliding over the surface of smooth paper, being sufficient to explode it. When moist, it decomposes slowly in contact with the air, yielding nitrogen, iodic acid, and hydriodic acid. A similar decomposition is produced more rapidly by boiling *water*, or by *alkaline solutions*. *Sulphydric acid* decomposes it, producing hydriodic acid, ammonia, and a deposit of sulphur. With *sulphurous acid*, it yields iodide of ammonium, hydriodic acid, and sulphuric acid. *Bromine-water* decomposes it instantaneously, *chlorine* more slowly: strong *nitric acid* attacks it violently. (Gladstone.)

This description applies to all the products obtained by the processes above-mentioned; nevertheless, these products are not absolutely identical in composition; but they all appear to be iodamides—that is to say, ammonia-molecules having the hydrogen more or less replaced by iodine—combined in some instances with ammonia itself. Gay-Lussac regarded the product of the action of iodine on ammonia as a compound of iodine and nitrogen alone, in fact, as tri-iodamide, NI^3, and, according to recent analyses by Stahlschmidt (see p. 281), this compound does appear to be formed under certain conditions; but repeated experiments by several chemists have shown that the explosive compound thus produced frequently also contains hydrogen: for when small portions of it in a state of perfect dryness are repeatedly exploded under a bell-jar, iodide of ammonium is deposited on the sides of the vessel.

According to Millon (Ann. Ch. Phys. [2] lxix. 78), the compound is mono-iodamide, NH^2I, and the decomposition just mentioned takes place as represented by the equation:

$$2NH^2I = NH^4I + I + N.$$

Bineau (*ibid.* [3] xv. 71), by determining the quantities of hydriodic acid, ammonia, and nitrogen produced in its decomposition by sulphydric acid, was led to adopt the formula, NHI^2, which is that of **di-iodamide**:

$$NHI^2 + 2H^2S = NH^4I + HI + S^2.$$

Gladstone (Chem. Soc. Qu. J. iv. 34) takes the same view of its constitution. By decomposing with sulphydric acid, the compound produced by the action of ammonia on an alcoholic solution of iodine, he finds that it contains 2 at. iodine to 1 at. nitrogen, while its decomposition by aqueous sulphurous acid is represented by the equation:

$$NHI^2 + 2SH^2O^3 + 2H^2O = NH^4I + HI + 2SH^2O^4.$$

He also finds that the formula NHI^2 is in accordance with the formation of the compound by the action of hypochlorite of calcium or iodide of ammonium (observed by **Playfair**), that reaction being attended with evolution of ammonia, according to the equation:

$$2ClCaO + 2NH^4I = NHI^2 + 2CaCl + 2H^2O + NH^3.$$

Bunsen (Ann. Ch. Pharm. lxxxiv. 1) has also examined the constitution of iodide of nitrogen, and arrived at different conclusions. He observes that the mode of formation of the explosive compound from iodine and ammonia, with hydriodic acid as the only secondary product, shows that it must be a substitution-product of ammonia, of the form NI^3, NHI^2 or NH^2I, associated at most with ammonia and hydriodic acid; 2. That it cannot contain hydriodic acid, because it dissolves in hydrochloric acid without evolution of gas, and forms a solution containing ammonia and protochloride of iodine, but no hydriodic acid; 3. That, to determine its composition, it is sufficient to ascertain how much ICl and how much NH^3 it yields with hydrochloric acid, and to see which of the following equations agrees with the results:

$$NI^3 + 3HCl = 3ICl + NH^3 \quad \ldots\ldots \quad (a)$$
$$NHI^2 + 2HCl = 2ICl + NH^3 \quad \ldots\ldots \quad (b)$$
$$NH^2I + HCl = ICl + NH^3 \quad \ldots\ldots \quad (c)$$
$$NH^2I + NH^3 + HCl = ICl + 2NH^3 \quad \ldots\ldots \quad (d).$$

Preparations obtained by mixing cold and more or less saturated anhydrous alcoholic solutions of iodine and ammonia, which were not decomposed by washing with absolute alcohol, gave, when dissolved in hydrochloric acid, quantities of ammonia, iodine, and chlorine, in the atomic proportion of 2 : 3 : 3, showing that the constitution of the compound thus formed was $NI^3.NH^3$. A preparation obtained by adding ammonia to a solution of iodine in nitro-muriatic acid diluted with water, and washed as quickly as possible with cold water, gave, with hydrochloric acid, quantities of ammonia and protochloride of iodine in the atomic proportion of 5 : 12, showing that its formula was $4NI^3.NH^3$. When washed with water for any length of time, even till the greater part of the compound was decomposed, with separation of iodine and nitrogen, the undecomposed portion still yielded more than 1 at. ammonia to 3 at. chloride of iodine, a proof that ammonia entered essentially into its constitution. Bunsen is of opinion that there exist two distinct compounds, $NI^3.NH^3$ and $4NI^3.NH^3$, formed in the manner shown by the equations,

$$2NH^3 + 6I = NI^3.NH^3 + 3HI$$
$$8(NI^3.NH^3) + 3H^2O = 2(4NI^3.NH^3) + 3(NH^4)^2O.$$

The formation of the so-called iodide of nitrogen by the action of ammonia on a solution of iodine in nitro-muriatic acid, would be inconsistent with this view, if that solution contained, not ICl, but, as is sometimes supposed, ICl^3, because NI^3 could not be formed from the latter. Bunsen has, however, shown that the solution of iodine in nitro-muriatic acid contains only ICl. The formation of the explosive compound from ICl is explained by the equation,

$$2NH^3 + 3ICl = (NI^3.NH^3) + 3HCl.$$

The immediate products of its explosion are nitrogen and hydriodic acid:

$$NI^3.NH^3 = N^2 + 3HI.$$

which latter is, for the most part, resolved by the high temperature into iodine and hydrogen, while another portion unites with the ammonia of the compound, forming iodide of ammonium, thereby setting free quantities of iodine and nitrogen equivalent to this ammonia.

The compound obtained by Bineau and by Gladstone, *viz.* di-iodamide NHI^2, is intermediate between the two compounds obtained by Bunsen:

$$2N^2I^3H^3 + N^5I^{12}H^3 = 9NHI^2$$

Bunsen's first compound $NI^3.NH^3$, may be represented as tri-iodammonammonium, $N\left\{\begin{matrix}H^2\\NHI^3\end{matrix}\right.$, and the second compound $4NI^3.NH^3$, might be formulated in a similar manner.

Lastly, it appears from the experiments of Stahlschmidt (Pogg. Ann. cxix. 421; Bull. Soc. Chim. de Paris 1864, p. 149), that di- or tri-iodamide may be produced according as alcoholic or aqueous ammonia is added to an alcoholic solution of iodine. By mixing alcoholic solutions of ammonia and iodine, he obtained a compound yielding by analysis quantities of iodine and nitrogen in the proportion of 2 at. I to 1 at. N, therefore NHI^2.

On the other hand, a product obtained by adding aqueous ammonia to an alcoholic tincture of iodine, yielded by decomposition with *sulphydric acid*, products containing 3 at. I to 1 at. N, according to the equation,

$$NI^3 + 3H^2S = NH^4I + 2HI + S^3.$$

The same substance treated with *iodide of methyl*, yielded in 24 hours, two layers of liquid, the upper consisting of aqueous hydriodic acid and iodide of ammonium, while the lower contained iodoform and penta-iodide of tetramethyl-ammonium:

$$2NI^3 + 3CH^3I = 2NH^3 + \underset{\text{Iodoform.}}{3CHI^3},$$

$$\text{and } 2NI^3 + 9CH^3I = 2HI + \underset{\text{Iodoform.}}{CHI^3} + \underset{\substack{\text{Penta-iodide}\\\text{of tetramethyl-}\\\text{ammonium.}}}{2N(CH^3)^4I^5}.$$

On treating the lower liquid with boiling absolute alcohol, a solution was obtained which deposited the penta-iodide in shining green crystals, while iodoform remained in the mother-liquor; and this mother-liquor being treated with potash, gave off ammonia and yielded iodoform, together with yellow crystals having the composition of di-iodomethylamide $N\left\{\begin{matrix}I^2\\CH^3\end{matrix}\right.$. The saline residue contained butyrate of potassium and other salts.

If the tri-iodamide used in the preceding reaction still retains ammonia, the products obtained are penta-iodide of tetramethylammonium, and a compound of 2 at. iodoform with mono-iodide of tetramethylammonium, $C^6H^{14}NI^7 = (CH^3)^4NI + 2CHI^3$.

By acting with ammonia on penta-iodide of tetramethylammonium (which contains 4 at. iodine in a state of less intimate combination than the fifth, and ready to act like free iodine), Stahlschmidt has obtained a compound containing $C^4H^{13}N^2I^5$, which may be regarded as a compound of di-iodamide, NHI^2, with tri-iodide of tetramethyl-ammonium. The same compound is formed on mixing alcoholic tincture of iodine with an ammoniacal solution of mono-iodide of tetramethyl-ammonium. It is a black powder, which explodes at 100°, or in contact with sulphuric acid, giving off nitrogen, and leaving the penta-iodide. The same decomposition takes place on heating its alcoholic solution. Sulphydric acid reduces it to mono-iodide of tetramethylammonium. Nitric acid decomposes it slowly. Heated with potash, it yields iodoform. It is insoluble in most liquids, but dissolves slightly in absolute alcohol. (Stahlschmidt.)

II. **Iodammonium.** NH^3I; or *Iodide of Ammonia*, $NH^3.I$.—Dry iodine absorbs dry ammonia-gas, 100 parts of iodine taking up 8·3 pts. of ammonia at + 10°, 9 pts. at 0°, and 9·4 pts. at—18°. The product is a blackish-brown very tenacious liquid, having a metallic aspect, smelling of ammonia and iodine, and imparting a brown stain to the skin and to paper. When heated, it gives off a portion of the ammonia and sublimes in violets vapours. Its lustre and tenacity are destroyed by excess of ammonia. It dissolves readily in alcohol, and is resolved by water into iodide of ammonium and di-iodamide:

$$2NH^3I = NH^4I + NH^2I.$$

In a current of hydrochloric acid gas, it is completely decomposed, yielding nitrogen gas, sal-ammoniac, iodide of ammonium, and free iodine. (Millon, Ann. Ch. Phys. lxix. 78.)

According to Bineau, 100 pts. iodine absorb 20·55 pts. ammonia-gas, yielding a product having the composition $N^3H^9I^2$. This may be represented as an *iodide of iod-ammon-ammon-ammonium* $\left[N\left\{\begin{matrix}H^3\\N\left\{\begin{matrix}H^3\\NH^3I\end{matrix}\right.\end{matrix}\right.\right].I.$

Millon's compound, if its composition has been correctly determined, is remarkable as presenting the only known instance of an ammonium-molecule existing in the free state.

III. **Iodide of Iodammonium.** $NH^3I^2 = (NH^3I).I$.—This compound, discovered by Guthrie (Chem. Soc. J. xvi. 239), is obtained: 1. By adding finely-powdered iodine to a saturated solution of nitrate or carbonate of ammonia mixed with about one-third of an equivalent quantity of potash. The iodine immediately liquefies, without perceptible rise of temperature, and unites with the elements of the ammonia, forming a very mobile brownish-black liquid, while the supernatant solution remains colourless. The iodide of iodammonium is separated by a pipette from the saline solution.—2. A similar, and probably identical liquid is obtained by adding to the solution of nitrate of ammonia, mixed with potash, a saturated solution of iodine in aqueous iodide of potassium.

Iodide of iodammonium dissolves in ether, alcohol, chloroform, sulphide of carbon, and aqueous iodide of potassium. When heated, it is partly resolved into iodine, and an iodiferous liquid, which may be distilled without decomposition, and is probably Millon's or Bineau's "iodide of ammonia."

$$NH^3I^2 = I + NH^3I.$$
$$3NH^3I^2 = I^4 + 3NH^3.I^2.$$

Exposed in the dry state to the air, it decomposes spontaneously into ammonia and iodine, no permanent gas being evolved. On agitating it in a eudiometer-tube with mercury, iodide of mercury is formed, and the mercury is depressed by the liberated ammonia, which latter is completely absorbed by water:

$$NH^3I^2 + 2Hg = NH^3 + 2HgI.$$

It is decomposed by water, colouring the water reddish-brown, from separation of iodine, evolving nitrogen gas, and yielding a residue of di-iodamide, which explodes spontaneously under water:

$$4NH^3I^2 + H^2O = 2NHI^2 + 2NH^4I + 2HI + H^2O = N^2 + 4HI + I^2 + 2NH^4I + H^2O$$

The formation of the di-iodamide is more rapid than its decomposition, so that some of it is left after the original compound is broken up.

The caustic *alkalis* effect the same decomposition as water, but more quickly, on account of the greater affinity of their metals for iodine.

Acids determine the formation of ammonia, *e. g.*:

$$NH^3I^2 + HCl = NH^4Cl + I^2.$$
$$NH^3I^2 + H^2SO^4 = (NH^4)^2SO^4 + I^2.$$

A portion of the compound prepared by the first method (p. 282) and decomposed in this way by dilute sulphuric acid, yielded in one experiment 5·92 per cent. NH^3 and 93·47 I, in another, 6·59 NH^3 to 63·04 I, the formula requiring 6·27 NH^3 to 93·73 I. On submitting the compound to fractional solution with chloroform, the residue was found to have exactly the same composition as the original substance, showing that the substance operated on was a definite compound, and not a mixture of two or more.

IODAMMONIUM. (See p. 282.)

IODANILINE. SYN. with IODOPHENYLAMINE. See PHENYLAMINE.

IODANISIC ACID. $C^8H^7IO^3$. Produced, together with hydriodate of oxanisamic acid, by the action of hydriodic acid on diazoanis-oxanisamic acid:

$$\underset{\text{Diazoanis-oxanisamic acid.}}{C^8H^6N^2O^3.C^8H^9NO^3} + 2HI = \underset{\text{Hydriodate of oxanisamic acid.}}{C^8H^9NO^3.HI} + \underset{\text{Iodanisic acid.}}{C^8H^7IO^3} + N^2$$

It forms white needles, insoluble in water, easily soluble in alcohol and in ether. The *silver-salt* is a white amorphous precipitate. (P. Griess, Proc. Roy. Soc. x. 309; Jahresber. 1859, p. 466.)

IODARSENIOUS ACID. See ARSENIC OXYIODIDE OF (i. 386).

IODATES. See IODINE, OXYGEN-ACIDS OF.

IODAURATES. See GOLD, IODIDES OF (ii. 929).

IODETHYLAMINE. See ETHYLAMINE (ii. 538).

IODETHYLENE. See ETHYLENE, IODATED (ii. 579).

IODHYDRIC ACID. See IODIDE OF HYDROGEN (p. 284).

IODHYDRINS. Compounds derived from glycerin or from glycide (ii. 896), by assumption of the elements of hydriodic acid and elimination of water. Only two have hitherto been obtained; both of which are glycidic ethers, viz.:—

Iodhydroglycide or Epi-iodhydrin . . $C^3H^5\left\}\begin{matrix}I\\O\end{matrix}\right. = C^3H^8O^3 + HI - 2H^2O.$

Iodhydrodiglycide (Berthelot's Iodhydrin) $\left.\begin{matrix}(C^3H^5)^2\\H\end{matrix}\right\}\begin{matrix}I\\O^3\end{matrix} = 2C^3H^8O^3 + HI - 3H^2O.$

The first has been already described (ii. 899). The second is obtained by saturating glycerin with hydriodic acid, keeping the liquid in a close vessel at 100° for forty hours, and then treating it with potash and ether. It is a syrupy liquid of a golden yellow colour, and specific gravity 1·783. It has a saccharine taste, dissolves about one-third of its bulk of water, but is not itself soluble in water. It is soluble in alcohol, and still more in ether. It is not volatile without decomposition. It burns without residue, giving off vapours of iodine. Potash decomposes it slowly at 100°, producing iodide of potassium, a liquid which appears to be identical with glycerin, and a volatile liquid, probably oxide of glyceryl $(C^3H^5)^2O^3$. The iodine in cod-liver oil is perhaps in the form of this, or a similar compound. (Berthelot and De Luca, Compt. rend. xxxix. 748.)

IODIDE OF ACETYL. See Acetyl (i. 35).—The iodides of other organic radicles are also described under the several radicles.

IODIDE OF ALUMINIUM. See Aluminium (i. 157).—The iodides of other metals are also described under the several metals.

IODIDE OF AMMONIA. See Iodammonium (p. 282).

IODIDE OF AMMONIUM. See Ammonium-Salts.

IODIDE OF BORON. See Boron (i. 627).

IODIDE OF HYDROGEN. IODHYDRIC or **HYDRIODIC ACID.** HI. Iodine does not combine with hydrogen at ordinary temperatures, even under the influence of sunshine; but when hydrogen gas and iodine vapour are passed together through a red-hot tube, combination takes place. According to Blundell (Pogg. Ann. ii. 216), spongy platinum brings about the combination at ordinary temperatures. The affinity of iodine for hydrogen is inferior only to that of oxygen, fluorine, chlorine, and bromine; consequently iodine separates hydrogen from most of its combinations, *viz.* from phosphoretted hydrogen, sulphydric acid, ammonia, and many organic compounds, *e.g.* alcohol, ether, and volatile oils, the result being in all cases the formation of hydriodic acid (Gaultier; Colin). Iodine does not decompose *water*, even at a red heat, or at all events, produces mere traces of iodic and hydriodic acids (Gay-Lussac). If, however, there is likewise present any substance that can take up the oxygen of the water, hydriodic acid is produced in abundance. Hence water and iodine, in contact with *phosphorus*, form hydriodic acid and phosphorous acid (Gay-Lussac): with *sulphurous acid*, only however when a considerable quantity of water is present, they yield hydriodic and sulphuric acids. With *sulphites*, if largely diluted, the products are hydriodic acid and a sulphate; similarly with *hyposulphites;* with *arsenious acid*, hydriodic acid and arsenic acid; with *stannous salts*, hydriodic acid and a stannic salt; and with certain *metals*, hydriodic acid and a metallic oxide.

Preparation.—1. *In the gaseous state.*—*a.* 1 pt. of phosphorus and 9 pts. of iodine are moistened with a small quantity of water, or covered with moistened glass-powder, and heated in a retort connected with a mercurial trough. Towards the end of the operation, hydriodate of phosphamine (p. 201) may sublime. Personne (Compt. rend. lii. 468) recommends the use of amorphous phosphorus for this purpose. The phosphorus is to be introduced into a tubulated retort, covered with a layer of water, and iodine added by successive portions, while the whole is gently heated. A regular stream of hydriodic acid-gas is then given off quite free from iodine-vapour.—*b.* 1 pt. of phosphorus is gently heated with 14 pts. of iodide of potassium, 20 of iodine, and a small quantity of water. If the evolution of gas becomes too violent, the vessel must be plunged into cold water; if it becomes too slow, heat must be again applied (Millon, J. Pharm. xxviii. 299):

$$4KI + I^{10} + P^2 + 7H^2O = K^4P^2O^7 + 14HI.$$

2. *In the liquid state.*—Iodine and persulphide of hydrogen, which, when they come in contact, unite, and form a yellowish-brown liquid, are placed together at the closed end of a dry glass tube; and at a short distance from them, in a bend of the tube, is placed a small quantity of water. If the tube be then sealed, and the first-mentioned liquid brought in contact with the water, decomposition takes place, resulting in the separation of sulphur and hydriodic acid, a considerable portion of the latter condensing in the liquid state. (Kemp, Phil. Mag. [3] vii. 444.)

3. *In aqueous solution.*—The aqueous acid may be prepared by passing the gas obtained by either of the preceding methods into water, which absorbs it very rapidly and in large quantity; or directly: 1. By distilling iodine with phosphorus and a large quantity of water.—2. By passing sulphydric acid gas into water in which iodine is diffused, the liquid being well agitated all the while, till the iodine has disappeared, and the liquid, which was brown at first, has become colourless; the liquid is then filtered and heated to commencing ebullition, in order to expel the excess of sulphydric

acid (Gay-Lussac). Since the sulphur, as it precipitates, envelopes the iodine which still remains undissolved, Le Royer and Dumas recommend the process of saturating water with iodine—decanting the liquid from the undissolved portion—converting the dissolved iodine into hydriodic acid, by means of sulphydric acid—digesting in this liquid a fresh portion of iodine, which dissolves much more abundantly in the hydriodic acid already produced—decanting again—once more saturating with sulphydric acid—again digesting with iodine, &c., &c. Another method is that of Stratingh, which consists in passing sulphydric acid gas through a solution of iodine in 16 pts. of alcohol, filtering, diluting with 32 pts. of water, and freeing the product by distillation from alcohol and excess of sulphydric acid. The acid prepared in this manner is liable, however, to be mixed with a product of disagreeable odour, arising from the action of the sulphydric acid on the alcohol.—3. Iodide of barium dissolved in water is exactly decomposed by the equivalent quantity of sulphuric acid, and the product is separated by filtration from sulphate of barium (Glover, Phil. Mag. [3] xix. 92).—4. Granulated lead is agitated with iodine and water till the liquid becomes colourless; sulphydric acid gas is then passed through, and the liquid decanted (Joss, J. pr. Chem. i. 133). The aqueous solution of the acid obtained by either of these methods may be concentrated by heating it in a retort.

Properties.—Hydriodic acid is a colourless gas, which reddens litmus strongly, and produces dense white fumes in moist air. It has a very sour suffocating odour, extinguishes flame, and is not itself combustible. Its specific gravity, according to Gay-Lussac's determination, is 4·4429, which shows that the gas is composed of equal volumes of hydrogen and iodine-vapour united without condensation; for the density thence deduced is $\frac{127 + 1}{2} = 64$ referred to hydrogen in unity, and $64 \times 0{\cdot}0693 = 4{\cdot}4352$ referred to air.

Hydriodic acid gas may be liquefied by pressure (p. 284). The liquid acid has a yellow colour, and solidifies at −51°, forming a transparent colourless mass intersected by fissures, like ice.

The aqueous acid smells like the gas; its taste is pungent at first, afterwards astringent and sour. When concentrated, it fumes strongly in the air. Its specific gravity and boiling-point vary with its strength. An acid containing 57·0 per cent. HI boils constantly at 127° under a pressure of 774 mm. A weaker or a stronger acid may be reduced to this strength by distillation under the ordinary pressure (in an atmosphere of hydrogen, to avoid decomposition). When dry hydrogen gas is passed through weaker or stronger acid, till the remaining acid attains a constant strength, this acid is found to contain from 60·3 to 60·7 per cent. HI, if the experiment is made at a temperature between 15° and 19°, and from 58·2 to 58·5 per cent. HI, if it has been performed at 100°. (Roscoe, Chem. Soc. J. xiii. 160.)

Decompositions.—1. A mixture of hydriodic acid and oxygen gases passed through a red-hot porcelain tube is resolved into water and iodine (Gay-Lussac). The aqueous solution undergoes a similar decomposition when exposed to the air, becoming brown from separated iodine.—2. The following compounds give up their oxygen to the hydrogen of the hydriodic acid, forming water and separating iodine. Hydrated *peroxide of hydrogen* is converted by it into water (Thénard). *Sulphurous anhydride* and hydriodic acid gases yield water, sulphur, and iodine:

$$SO^2 + 4HI = 2H^2O + S + I^4.$$

If water is present, the two acids have no action on one another (Dumas). Hydriodic acid gas, or its concentrated aqueous solution, is decomposed by strong *sulphuric acid*, yielding water, sulphurous acid, and free iodine:

$$H^2SO^4 + 2HI = H^2O + H^2SO^3 + I^2.$$

On the addition of water, sulphuric acid and hydriodic acids are reproduced. Aqueous *iodic acid* and hydriodic acid yield water and iodine:

$$HIO^3 + 5HI = 3H^2O + I^6.$$

Hypochlorous acid decomposes hydriodic acid, both in the gaseous form and in the state of aqueous solution (Balard). *Nitric acid* yields iodine, water, and nitric oxide (Gay-Lussac). *Ferric salts* are converted by hydriodic acid into ferrous salts, iodine being at the same time precipitated (Gay-Lussac).—3. *Chlorine gas*, in small quantity, converts hydriodic acid gas into hydrochloric acid and iodine:

$$Cl + HI = HCl + I;$$

in larger quantity, into hydrochloric acid and trichloride of iodine; *e.g.*

$$4Cl + HI = HCl + ICl^3.$$

(Gay-Lussac). In a similar manner, *bromine* and hydriodic acid gas yield hydrobromic acid gas and iodine, the action being attended with evolution of heat (Balard). Hence hydriodic acid imparts a blue colour to starch on the addition of chlorine or bromine (not in excess), or of sulphuric, nitric, or iodic acid, or a mixture of hydrochloric acid and chlorate of potassium.—4. *Potassium, zinc, iron, mercury*, and other metals, immersed in this gas, are converted into iodides, 1 volume of hydrogen being at the same time liberated from 2 volumes of hydriodic acid gas (Gay-Lussac).—5. With most *basic metallic oxides*, hydriodic acid forms water and a metallic iodide. Some of these iodides separate immediately, so that, with the salts of certain metallic oxides, aqueous hydriodic acid forms precipitates consisting of metallic iodides, and distinguished by the following colours: Oxide of bismuth, brown; oxide of lead, orange-yellow; mercurous oxide, greenish-yellow; mercuric oxide, scarlet; oxide of silver, yellowish-white. Other metallic iodides remain dissolved in the liquid, and in that state may be regarded as hydriodates of metallic oxides. With *metallic peroxides*, *e.g.* the peroxide of manganese or of lead, hydriodic acid forms a metallic iodide (or hydriodate), water, and free iodine; *e.g.*

$$Pb^2O + 2HI = 2PbI + H^2O + I.$$

With many *organic compounds*, hydriodic acid reacts in the same manner as with inorganic compounds, sometimes deoxidising them, with formation of water and elimination of iodine, sometimes simply exchanging its hydrogen for a radicle of the organic compound. Examples of the first mode of action are afforded by *mannite*, with which hydriodic acid yields iodide of hexyl, water, and iodine (p. 154), and by *erythromannite*, with which it yields in like manner iodide of tetryl (ii. 505). An instance of the second mode of action is exhibited by *salicylate of methyl* (wintergreen oil), with which hydriodic acid forms iodide of methyl and salicylic acid. (Lautemann, Ann. Ch. Pharm. cxxv. 13.)

$$C^7H^5(CH^3)O^3 + HI = CH^3I + C^7H^6O^3.$$

It is by reactions of this kind that Matthiessen and Foster (Chem. Soc. J. xvi. 358) have shown that cotarnine and its derivatives are methylised compounds. (See Cotarnine, ii. 90; Hemipinic acid, iii. 142; Opianic acid, and Narcotine.)

Hydriodic acid unites directly with ammonia, phosphamine, and other organic amines, phosphines, arsines, stibines, &c., forming salts, which may be regarded either as hydriodates of these ammonia-derivatives, or as iodides of the corresponding derivatives of ammonium, *e.g.* hydriodate of triethylamine, $N(C^2H^5)^3.HI$, iodide of triethylammonium, $[N(C^2H^5)^3H]I$. Similarly with other organic bases.

It likewise unites directly with many hydrocarbons containing even numbers of hydrogen-atoms; the olefines and camphenes, for example. Greville Williams, by distilling the hydrocarbons obtained from Boghead naphtha with fuming hydriodic acid, obtained compounds which might be regarded as hydriodates of olefines, $C^nH^{2n}.HI$, or as iodides of the corresponding monatomic alcohol-radicles, $C^nH^{2n+1}I$, as when treated with alcoholic ammonia, they yielded the hydriodates of the corresponding amines, $C^nH^{2n+3}N.HI$. The hydriodates of the olefines are not, however, in all cases identical with the corresponding monatomic alcoholic iodides; hydriodate of amylene, for example, is merely isomeric with iodide of amyl; for when treated with moist oxide of silver, it yields a hydrate of amylene, not exhibiting the properties of common amylic alcohol. Similarly with hydriodate of hexylene (p. 188).

IODIDE OF NITROGEN. See Iodamides (p. 280).

IODIDES, METALLIC. These compounds are obtained by the same processes that yield the chlorides and bromides.

1. By the direct action of iodine on a metal, frequently even at ordinary temperatures, as in the case of mercury. The combination is attended with development of heat, sometimes with flame, which is coloured violet by the iodine vapour (*e.g.* potassium sodium).

2. By the action of iodine on certain metallic oxides, hydrates, or carbonates. Iodine displaces the oxides of potassium, sodium, barium, and calcium at a red heat, and that of oxide of silver at ordinary temperatures. When solutions of caustic or carbonated alkali are treated with iodine, mixtures of iodide and iodate are produced, which last salt is decomposed by heat into iodide and oxygen. Iodine and peroxide of barium, when mixed with water, decompose into iodide of barium and oxygen, thus:

$$I^2 + Ba^2O^2 = 2BaI + O^2.$$

3. By the action of certain metals, such as potassium, zinc, and iron, on hydriodic acid, the metal then replacing the hydrogen.—4. By saturating hydriodic acid with oxides, hydrates, or carbonates. With a peroxide and hydriodic acid, iodine is liberated.—5. The insoluble iodides are prepared by adding hydriodic acid or the solution of a metallic iodide to solutions of the heavy metals.

All iodides are destitute of metallic lustre; some of them are very beautifully coloured. Their specific gravity is often lower than the mean specific gravity of their constituents: such is the case with the iodides of potassium, lead, copper, and silver. (Boullay.)

But few metallic iodides are decomposed by heat alone; the iodides of gold, silver, platinum, and palladium, however, give up their iodine when heated. Most metallic iodides when ignited in open vessels, so that the air has excess to them, give up their iodine, and are converted into oxides; such, however, is not the case with the iodides of potassium, sodium, bismuth, and lead. *Chlorine*, at red heat, decomposes the metallic iodides, converting them into chlorides, and either setting the iodine free or forming chloride of iodine. *Bromine* acts in a similar manner. Chlorine-water likewise liberates the iodine. *Hydrochloric acid* gas decomposes metallic iodides at a red heat, forming hydriodic acid gas and a metallic chloride. Concentrated *sulphuric* and *nitric acid* and likewise *acid sulphate* of *potassium* decompose all metallic iodides on the application of heat, the products being iodine, which escapes in violet vapours (which give a blue colour to paper moistened with starch), and a sulphate or nitrate of the corresponding metal. When this change is produced by nitric acid, pernitric oxide is formed at the same time; sulphuric acid and acid sulphate of potassium evolve sulphurous anhydride, sometimes also sulphydric acid. Sulphuric acid or acid sulphate of potassium with peroxide of manganese, peroxide of lead, or chromate of potassium, produces the same decomposition, but without evolution of sulphurous anhydride. A bead of microcosmic salt saturated with *oxide of copper* communicates a beautiful green colour to the blow-pipe flame on the addition of a metallic iodide (Berzelius). Metallic iodides agitated with sulphuric acid and *sulphide of carbon*, communicate an amethyst-red tint to the latter.

Very few metallic iodides remain unaltered in contact with *water:* such, however, is the case with the iodides of bismuth, lead, copper, and several of the noble metals. Some of them are converted by water into an oxide, which is precipitated, and hydriodic acid which dissolves in the water (iodide of tin): or into a precipitated compound of iodide and oxide of the metal, and a solution of the iodide in aqueous hydriodic acid (the iodides of antimony and tellurium). Most metallic iodides are perfectly soluble in water; and the solution may be regarded as containing either the unaltered iodide, or a hydriodate of the oxide formed by double decomposition (*e.g.* the iodides of the alkali-metals, iron, nickel, cobalt, &c.).

The soluble iodides are extremely poisonous. When evaporated out of contact of air, they generally leave anhydrous metallic iodides, which partly separate in the crystalline form before the water is wholly driven off. The earthy hydriodates, however, are resolved, on evaporation, into the earthy oxides and hydriodic acid, which escapes. A very small quantity of *chlorine* colours the solution yellow or brown, by partial decomposition; and a somewhat larger quantity takes up the whole of the metal, forming a chloride (or hydrochlorate), and separates the iodine, which then gives a blue colour with starch; a still larger quantity of chlorine gives the liquid a paler colour, and converts the separated iodine into trichloride of iodine, which does not give a blue colour with starch, and frequently enters into combination with the chloride produced. Strong *sulphuric acid* and somewhat concentrated *nitric acid* colour the solution yellow or brown; and if the quantity of the iodide is large, and the solution much concentrated or heated, they liberate iodine, which partly escapes in violet vapours. *Starch* mixed with the solution, even if it be very dilute, is turned blue—permanently, when the decomposition is effected by sulphuric acid; for a time only when it is effected by nitric acid, especially if that acid be added in large quantity. If the sulphuric acid contains sulphurous acid, which is very likely to be the case with fuming oil of vitriol, it does not produce the blue colour, even when added in large excess. If a liquid in which iodine is present (urine, for example) contains much organic matter, which may decompose the sulphuric acid and form sulphurous acid, it will not produce the blue colour with starch and sulphuric acid unless it be diluted with water (Dupasquier, J. Pharm. 28, 218). If the solution likewise contains a salt of *iodic acid*, most acids produce a brown colour and separate iodine; because, by virtue of their affinity for the base of the iodate, they facilitate the mutual decomposition of the hydriodic and iodic acid: $IHO^3 + 5HI = 3H^2O + 3I^2$. The separation of iodine, and the blueing of the starch likewise takes place on adding hydrochloric acid to the solution, together with a stannic, ferric, or cupric salt, or a salt of chromic acid. Also, if the solution of the iodide be covered with gelatinous starch, the negative pole of a small voltaic battery immersed in the former, and the positive pole in the latter, the starch is turned blue in the neighbourhood of the positive wire, even if the solution contains a much larger quantity of bromide or chloride than of iodide (Steinberg, J. pr. Chem. xxv. 288). If the aqueous solution of a metallic iodide contains only $\frac{1}{10,000}$ part of iodine, it gives a strong blue colour with dilute gelatinous starch, on the addition of aqua-regia: with $\frac{1}{100,000}$ part of iodine, the precipitate is violet; with $\frac{1}{200000}$, rose-coloured; and with $\frac{1}{500000}$, a pale rose-colour is produced after the lapse of a few hours (Harting, J. pr. Chem. xxii. 46). If the solution likewise contains a large quantity of metallic chloride, the blueing of the starch is not readily produced by the addition of nitric acid, in consequence of the formation of chloride of iodine: in this case, a solution of starch in boiling dilute sulphuric acid may be added to the solution of the iodide, and then a very small quantity of chlorine water, the liquid being stirred at the same time. (Berzelius.)

The aqueous solution of an iodide gives a brown precipitate with salts of *bismuth;* orange-yellow with *lead-salts;* dirty-white with *cuprous* salts, and also with *cupric* salts, especially on the addition of sulphurous acid; greenish-yellow with *mercurous* salts; scarlet with *mercuric* salts; yellowish-white with *silver*-salts; lemon-yellow with *gold*-salts; brown with *platinic* salts, first however turning the liquid dark brown-red; and black with salts of *palladium*, even when extremely dilute. All these precipitates consist of metallic iodides, many of them soluble in excess of the soluble iodide: the silver precipitate is insoluble in nitric acid and very little soluble in ammonia.

When iodine is added to an aqueous solution of a salt of hydriodic acid, the liquid takes up an additional quantity of iodine, equal, according to Baup (J. Pharm. ix. 46) to that which it already contains. It thereby acquires a dark-brown colour, and is supposed by some chemists to contain a *metallic polyiodide* or a salt of *hydriodous acid;* but the affinity by which the iodine is retained is very feeble.

Many metallic iodides absorb *ammonia* in definite proportions, forming compounds which may be regarded as iodides of ammonium-molecules, having part of the hydrogen replaced by a metal.

Some of these compounds unite with the *oxides* of the corresponding metals, forming oxyiodides, *e.g.* antimony and tellurium.

Metallic iodides also unite with one another, forming double iodides or iodine-salts.

IODIDES, ORGANIC. 1. *Acid.*—The iodides of acid organic radicles have not been much studied. Iodide of acetyl, C^2H^3OI, is obtained by the action of iodide of phosphorus on acetate of potassium or acetic anhydride; and iodide of benzoyl, C^7H^5OI, by the action of iodide of potassium on chloride of benzoyl. These acid iodides resemble the corresponding chlorides, but are much more easily decomposible.

2. *Alcoholic Iodides, Iodhydric* or *Hydriodic ethers.*—The monatomic alcoholic iodides are produced by the action of hydriodic acid, or iodide of phosphorus, on the corresponding alcohols, and by that of hydriodic acid on the corresponding diatomic hydrocarbons, *e.g.* iodide of amyl, $C^5H^{11}I$, from amylene, C^5H^{10}, and hydriodic acid. It is doubtful, however, whether the iodides obtained by this last process are really identical, or only isomeric with those obtained from the alcohols (p. 286).

The monatomic alcoholic iodides are less stable than corresponding chlorides, sometime decomposing under the influence of *light*, into the alcohol-radicle and free iodine, *e.g.* iodide of ethyl.

Heated in sealed tubes with certain metals, viz. *zinc*, *potassium*, or *sodium*, they yield a metallic iodide and the alcohol-radicle: *e.g.* zinc with iodide of ethyl; potassium or sodium with iodide of tetryl. With *mercury*, *tin*, *lead*, *arsenic*, *antimony*, and a few other metals, under the influence of heat, or of the sun's rays, they yield the iodides of organo-metallic bodies; thus, iodide of ethyl, enclosed in a sealed tube with strips of tinfoil, and heated in a sealed tube to 180°, or exposed to the sun's rays concentrated by a lens or mirror, yields iodide of stannethyl, $(C^2H^5)^2SnI^2$ (ii. 235). Sometimes the organo-metallic compound thus formed acts further on the iodide, giving rise to new products (ii. 533, 535). Similar reactions take place when the alcoholic iodides are heated with the arsenides, antimonides, stannides, &c. of potassium or sodium, the organo-metallic radicles being then formed with greater facility, because the alkali-metal unites with the iodine.

The alcoholic iodides, heated in sealed tubes with *ammonia*, yield a mixture of the iodides of various ammonium-bases, in which the hydrogen of the ammonium is more or less replaced by the alcohol-radicle; thus, iodide of methyl with ammonia yields a mixture of the iodides of ammonium, and of methyl-, dimethyl-, trimethyl-, and tetramethyl-ammonium. With *primary* and *secondary monamines*, they react in a similar manner, the reaction becoming less complex as the amine itself is of a higher order. With *tertiary monamines* they unite directly, yielding the iodides of ammonium-bases in which the hydrogen is wholly replaced by the alcohol-radicle, *e.g.*

$$\underset{\text{Triethylamine.}}{(C^2H^5)^3N} + \underset{\text{Iodide of ethyl.}}{C^2H^5I} = \underset{\text{Iodide of tetrethylammonium.}}{(C^2H^5)^4NI}$$

Similarly with tertiary *phosphines*, *arsines*, *stibines*, &c.

Alcoholic iodides treated with *potassium-* or *sodium-alcohols* yield the oxides of alcohol-radicles, thus:

$$\underset{\substack{\text{Iodide of}\\\text{ethyl.}}}{C^2H^5I} + \underset{\substack{\text{Ethylate of}\\\text{sodium.}}}{C^2H^5NaO} = NaI + \underset{\substack{\text{Ethylic}\\\text{oxide.}}}{(C^2H^5)^2O}$$

$$\underset{\substack{\text{Iodide of}\\\text{methyl.}}}{CH^3I} + \underset{\substack{\text{Ethylate of}\\\text{sodium.}}}{C^2H^5NaO} = NaI + \underset{\substack{\text{Methyl-ethylic}\\\text{oxide.}}}{CH^3.C^2H^5.O}$$

With *silver-salts of organic acids*, they yield compound ethers, *e.g.*:

$$\underset{\substack{\text{Iodide of}\\\text{ethyl.}}}{C^2H^5I} + \underset{\substack{\text{Acetate of}\\\text{silver.}}}{\left.\begin{matrix}C^2H^3O\\Ag\end{matrix}\right\}O} = AgI + \underset{\substack{\text{Acetate of}\\\text{ethyl.}}}{\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O}$$

The facility with which the alcoholic iodides are decomposed by these several reagents renders them peculiarly well adapted to the preparation of other compounds of the alcohol-radicles.

Diatomic Alcoholic Iodides.—The iodides of the olefines, $C^nH^{2n+2}I^2$, which are the only known compounds of this group, are produced by direct combination; also by passing the vapours of the corresponding monatomic alcoholic iodides through a red-hot tube; *e.g.*:

$$2C^2H^5I = C^2H^4I^2 + C^2H^4 + H^2;$$

and by the action of hydriodic acid on the diatomic alcohols (ii. 578). The few which have been prepared are crystalline solids, easily resolved into iodine and the diatomic alcohol-radicle, the decomposition taking place slowly, even at ordinary temperatures. They are completely decomposed by *alcoholic potash*, yielding iodated hydrocarbons; *e.g.*, iodide of ethylene, $C^2H^4I^2$, is resolved into hydriodic acid, HI, and iodethylene, C^2H^3I. Their reactions with *ammonia* have not been much examined, but they appear to be similar to those of the corresponding bromides. (See ETHYLENE-BASES, ii. 585.)

3. The *organo-metallic iodides* resemble the corresponding bromides and chlorides; they are obtained in the manner above described by the action of metals and alloys on the alcoholic iodides under the influence of heat or light.

IODIDES OF NITROGEN. See IODAMIDES (p. 208).

IODIDES OF PHOSPHORUS, SELENIUM, SULPHUR, and **TELLURIUM.** See these several elements.

IODINE. *Atomic weight*, 127. *Symbol*, I.—This element was discovered in 1812, by M. Courtois, of Paris, in the mother-liquor of kelp from which carbonate of soda had been prepared. Its chemical properties were examined by Clement and Desormes (Ann. Chim. lxxxviii. 304), and afterwards more completely by Davy (Phil. Trans. 1814, i. 74) and Gay-Lussac (Ann. Chim. lxxxviii. 311, 319; xci. 5). Its name is derived from the Greek word ἴον (violet), on account of the colour of its vapour.

Iodine exists in many salt-springs and other mineral waters; also in sea-water, which is the great source of it. The proportion of iodine in sea-water is, however, so minute, that it can only be detected by operating upon very large quantities; but it becomes stored up in the bodies of marine plants and animals, especially in certain algæ, the *Fucus palmatus*, for example. These plants are collected on the coast of Scotland, Jersey, and other places, and burnt to ashes in a shallow pit to form kelp or varec, a substance which was formerly valued chiefly for the carbonate of sodium that it yielded; but now that this salt is more economically manufactured from chloride of sodium, kelp is chiefly valued for the chloride of potassium and the iodine obtained from it, especially the latter. Iodine exists in kelp in the form of iodide of potassium and iodide of sodium, which, being much more soluble than the other constituents, remain in the mother-liquor after the carbonates and chlorides have crystallised out.

Iodine has also been found in certain land-plants; *e.g.*, in tobacco, and in a species of *Salsola*, growing in the floating gardens on the fresh-water lakes near the city of Mexico.

Various marine animals also contain iodine, viz., the common sponge, the horse-sponge; various species of *Sertularia*, *Tubularia*, *Rhizostoma*, *Cyana*, *Doris*, *Venus*, and oysters. It is also contained in cod-liver oil, the pale oil containing, according to De Jongh, 0·0374 per cent. iodine, the pale brown oil 0·0406, and the brown oil 0·0295 per cent.

Iodine is likewise found in several minerals, *viz.*, as iodide of mercury and iodide of silver; as iodide of potassium, sodium, or magnesium, in Chili saltpetre; as iodide of calcium or magnesium in certain dolomites; in the rock-salt of Halle in the Tyrol, probably in the form of iodide of sodium; and sublimes as iodide of ammonium, together with sal-ammoniac, in the burning coal-mine of Commentry.

Iodide of ammonium has been found in gas-water, in the coke left in the retorts, and in the ashes of coal and peat from various localities.

Chatin (Compt. rend. xxx. 352; xxxi. 280; xxxii. 669; xxxiii. 519, 529, 581) has found iodine in the waters of various streams and rivers, in quantity increasing with the proportion of iron present, and more abundantly in the waters of volcanic districts than in those from the oolitic and limestone formations; also in the rain-water of Paris, Pisa, Florence, and other localities; but none in the rain-water of mountainous districts. He also states that it is sometimes present in the air in certain localities; but **Lohmeyer** (Phil. Mag. [4] vi. 237), **Macadam** (Chem. Soc. Qu. J. vi. 166) and others have failed to detect its presence in the air. Macadam has found iodine in commercial potash, in various samples of alkaline carbonates (used as reagents) in the ashes of wood-charcoal, in coals, and in numerous plants.

Preparation.—I. From *varec* or *kelp*. The material is exhausted with hot water; the solution is freed as much as possible, by evaporation and cooling, from the crystallised salts contained in it (chloride of potassium, chloride of sodium, carbonate of sodium, sulphate of sodium, &c.); and the mother-liquor—which, besides iodide of sodium, still contains sulphide and hyposulphite of sodium, and a portion of the salts already mentioned*—is subjected to one of the following processes: 1. It is heated in a subliming apparatus with oil of vitriol:

$$2NaI + 2H^2SO^4 = Na^2SO^4 + 2H^2O + SO^2 + I^2.$$

This method is not very advantageous, because the sulphurous acid evolved acts upon the iodine and the water which is present, in such a manner as to produce hydriodic and sulphuric acids. (**Soubeiran.**)

2. The mother-liquor is heated in a subliming apparatus with peroxide of manganese and sulphuric acid (**Wollaston**):

$$2NaI + 2H^2SO^4 + Mn^2O^2 = Na^2SO^4 + Mn^2SO^4 + 2H^2O + I^2.$$

Mr. Whytelaw, of Glasgow, adds one measure of oil of vitriol, carefully and in small portions at a time, to eight measures of the mother-liquor contained in a leaden boiler —whereupon, carbonic anhydride and sulphydric acid (from the sulphide of sodium) are first evolved; and, after exposure to the air for a day or two, sulphurous anhydride (from the hyposulphite of sodium) escapes, and sulphur is precipitated. He then pours off the liquid from the crystallised sulphate of sodium into a leaden cylinder placed horizontally in a sand-bath, and fitted with a head, the beak of which passes into the first of three tubulated receivers luted one into the other; heats the mixture to 65° C. (149° F.); and, after adding the peroxide of manganese and putting on the head, gradually raises the temperature to 100°, but not higher, because at 118° C. (244° F.) chloride of iodine begins to distil over. Sometimes also cyanide of iodine collects in the last receiver in white, needle-shaped crystals. The liquid which remains in the retort still contains iodine, and on cooling, deposits crystals of iodide of lead and double iodide of lead and sodium.

3. The mother-liquor is evaporated to dryness, the residue heated with peroxide of manganese, and the iodine precipitated from the filtered solution by chlorine. This is **Barruel's** method, which is carried out as follows:—The residue obtained by evaporating the mother-liquor to dryness is mixed with $\frac{1}{10}$ of its weight of peroxide of manganese, and the mixture heated in an iron vessel to commencing redness (stirring all the while), but not high enough to cause the evolution of vapours of iodine; the heat is continued till a sample of the mixture treated with sulphuric acid no longer evolves sulphydric acid or deposits sulphur; that is to say, till the whole of the sulphide and hyposulphite of sodium are converted into sulphate. The mass is then dissolved in such a quantity of water that the solution may have a density corresponding to 36° of Baumé's hydrometer; chlorine gas is passed through the filtered liquid, which is constantly stirred, till a sample treated with more chlorine no longer gives a precipitate of iodine (excess of chlorine would convert the iodine into chloride and redissolve it), and the pulverulent precipitate of iodine is collected on a filter, and purified by sublimation. Mohr is of opinion that a loss of iodine may occur in this process during the heating of the evaporated residue with manganese.

4. The mother-liquor is precipitated by a copper-salt and metallic iron, and the cuprous iodide heated with peroxide of manganese (**Soubeiran**). The mother-liquor is diluted with water, and mixed with a solution of sulphate of copper, as long as any precipitate is produced:

$$2NaI + Cu^2SO^4 = Na^2SO^4 + Cu^2I + I;$$

the liquid containing the free iodine is separated by decantation and washing from the precipitated cuprous iodide, and mixed with sulphate of copper and iron filings till it no longer smells of iodine:

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* A mother-liquor from *varec*, examined by Soubeiran, contained no carbonate or sulphate; the principal salts contained in it, in addition to the iodides, were the nitrates of calcium and magnesium.

$$I + Cu^2SO^4 + Fe^2 = Cu^2I + Fe^2SO^4;$$

and the cuprous iodide thus produced is quickly separated by elutriation from the excess of iron-filings and from the liquid, before the ferrous sulphate has time to oxidate in the air. The two portions of iodide, obtained as above, are next dried at a gentle heat (a stronger heat would decompose the cuprous iodide, since it is mixed with basic ferric sulphate, and evolve iodine); the whole is mixed with twice or three times its weight of peroxide of manganese, and a sufficient quantity of sulphuric acid to form it into a paste; and the mixture is strongly heated in a subliming apparatus:

$$Cu^2I + Mn^2O^2 + 2SH^2O^4 = Cu^2SO^4 + Mn^2SO^4 + I;$$

or the sulphuric acid is dispensed with, and a stronger heat applied:

$$2Cu^2I + 3Mn^2O^2 = Cu^2O + 2Mn^2O^3 + I^2.$$

In both cases, the iodine which passes over is accompanied by water derived from the hydrated cuprous iodide, from the sulphate of calcium precipitated with it, and from the sulphuric acid when it is used in the process. This water holds in solution a portion of the iodine, which may be again precipitated by sulphate of copper. By this process, 100 pts. of the mother-liquor yield 1 pt. of iodine.

II. *From the mother-liquor of the Caliche of Peru.*—This mother-liquor contains, according to Reichardt's analysis:

Nitrate of sodium	23·300
Chloride of sodium	8·594
Sulphate of magnesium	2·214
Chloride of magnesium	1·121
Iodate of sodium	0·440
Water, given off at 100°	57·406
Combined water (and loss)	6·925
	100·000

According to Grüneberg (J. pr. Chem. lx. 172), part of the iodine in this liquid is in the form of iodide of magnesium, which is decomposed, during the evaporation, into magnesia and hydriodic acid, thereby occasioning loss of iodine; this however may be prevented by the addition of caustic soda. The liquor is then treated with iron filings and sulphate of copper (as in Soubeiran's method) till the whole of the iodine is precipitated as ferrous and cuprous iodide:

$$\underset{\substack{\text{Iodate of}\\\text{sodium.}}}{2NaIO^3} + Cu^2SO^4 + Fe^{14} = Cu^2I + Fe^2I + Fe^2SO^4 + 5Fe^2O + Na^2O;$$

and the precipitate, which also contains oxychloride of copper, is distilled with peroxide of manganese and sulphuric acid. The receiver contains crystals of iodine and chloride of iodine. The latter is heated with carbonate of potassium, which separates all the iodine, with formation of chloride and chlorate of potassium.

Jacquelin and Favre extract the iodine from the mother-liquors of caliche and commercial nitrate of sodium, by the following process, founded on the action of sulphurous acid on the iodates:

$$2MgIO^3 + 5H^2SO^3 = Mg^2SO^4 + 4H^2SO^4 + H^2O + I^2.$$

The solution of the nitre having been concentrated to 36° or 37° Bm., a sample of it is mixed with aqueous sulphurous acid, cautiously and with constant stirring, until all the iodine is precipitated; the quantity of sulphurous acid used is then noted; and from the data thus obtained, the manufacturing operations are managed.

The solution of the nitre is run into a cistern built of stone or fire-bricks, and closed with a cover coated on the under side with glass plates. The cistern is fitted with an agitator, having stoneware arms worked from above through the cover, while the solution of sulphurous acid is being mixed with the liquid. The iodine which precipitates is collected, washed, and sublimed as above.

If the iodine is present in the form of iodide and iodate together, both chlorine and sulphurous acid must be employed, the necessary quantities having been previously ascertained by test-samples. If the iodate is present in the largest proportion, the chlorine-water is first used, and then the aqueous sulphurous acid; but when the iodate is the chief ingredient, the order of treatment is reversed.

III. *From Mineral waters.*—The quantity of iodine existing in certain mineral waters and in spent artificially iodised baths may be extracted by means of charcoal, which completely precipitates free iodine on the surface of its particles, where it remains fixed like a dye upon cloth, and cannot be removed by heat, by chlorine, or by water or alcohol either hot or cold. Animal charcoal acts most powerfully, but lamp-black is recommended for the purpose on account of its cheapness and its state of fine division. The water containing the iodine-compound having been treated with a mixture of 1 pt. sulphuric to 2 pts. nitric acid, to set the iodine free, is run on to a filter filled with charcoal, and the charcoal thus iodised is placed upon another filter, where it is mixed with hydrated protoxide of iron, whereby the iodine is converted into soluble iodide of iron, which may be obtained in the solid state by evaporating in a current of hydrogen, or distilled with peroxide of manganese and sulphuric acid in the usual way, to obtain iodine.

Purification.—The iodine obtained by either of the preceding processes may be purified by washing with a small quantity of water, pressing between paper, drying and subliming a second time. According to Serullas, the iodine of commerce may be completely purified by solution in alcohol, filtration, and precipitation with water.

For further details relating to the manufacture of iodine, see *Richardson and Watts's Chemical Technology*, vol. i. part 3, pp. 562–575.

Properties.—Iodine is at ordinary temperatures a crystalline solid, having a greyish-black colour and metallic lustre, like plumbago or specular iron-ore. It is transparent only in very thin slices, and then appears red by transmitted light. It is very soft, and easily pulverised. It crystallises by sublimation in large brilliant, rhomboïdal plates, or in elongated octahedrons. Finer crystals are obtained from solution, as by exposing to the air an aqueous solution of hydriodic acid, or a solution of iodine in ether. The crystals belong to the trimetric system, having their axes in the ratio of 4 : 3 : 2.

Iodine melts at 107° C. (224·6 F.), and solidifies in a lamellated mass on cooling. It boils (when immersed in strong sulphuric acid) between 175° and 180° C. (347°–356° F.). In the open air it volatilises at ordinary temperatures, especially when moist, diffusing an odour having considerable resemblance to that of chlorine, but easily distinguished from it. Its vapour has a splendid violet colour (hence the name of the substance). The saturated vapour is so deep-coloured, that a stratum four inches thick is impervious to daylight or candlelight. The colour is seen to great advantage when a quantity of iodine is thrown upon a hot brick. Iodine-vapour is one of the heaviest of gaseous bodies, its specific gravity referred to air as unity being 8·716 according to the experiments of Dumas, and $127 \times 0·0693 = 8·801$ by calculation from the atomic weight.

Iodine dissolves but sparingly in *water*, 1 pt. of iodine requiring 7,000 pts. of water to dissolve it at ordinary temperatures. *Alcohol* and *ether* dissolve it more readily, forming dark brown liquids. The alcoholic solution yields crystals of iodine by evaporation, and is decomposed by water, which throws down the iodine as a brown powder. Iodine also dissolves with facility in water containing soluble *iodides*, or *nitrate* or *chloride of ammonium*, the solutions having a deep red colour. A liquid containing 20 grains of iodine and 30 grains of iodide of potassium in an ounce of water, is known as Lugol's solution, and is preferred in medicine to the alcoholic tincture, because it is not decomposed by dilution with water. Iodine is soluble in *sulphide of carbon*, a very small quantity of it being sufficient to impart to the liquid a very rich violet tint.

Iodine in its chemical reactions resembles chlorine and bromine, but is less energetic, and is displaced from most of its combinations by either of those bodies. It destroys colouring matters but slowly, and does not decompose water under the influence of the sun's rays. It exerts a destructive action on organic tissues, producing a deep yellow brown stain on the skin, paper, &c. This colour disappears after a while under the influence of heat, if the contact has not been too much prolonged.

Iodine forms with *starch* a compound of a deep blue colour, soluble in pure water, but insoluble in acid and alkaline solutions. Its production affords an exceedingly delicate test of the presence of iodine. If the iodine is in the free state, the blue colour is at once produced, but if it is in combination as a soluble iodide, no coloration takes place till the iodine is liberated by chlorine or nitrous acid (see IODIDES, METALLIC, p. 287). The blue compound is decolorised at a temperature of 70° or 80° C. (158°–176° F.), but recovers its colour as the liquid cools.

Iodine is employed in the laboratory for many chemical preparations, and as a test for starch. It was first introduced into medicine by Coindet of Geneva, who employed it with success for the treatment of goitre, either dissolved in alcohol, or in solution of iodide of potassium, or as iodide of sodium; and since that application, most mineral waters to which the virtue of curing goitre was ascribed, have been found to contain iodine (Boussingault, Ann. Ch. Phys. liv. 163). On the other hand, Lohmeyer (Phil. Mag. [4] vi. 237) failed to detect iodine in the air and water of certain mountainous districts which are peculiarly free from goitre. Iodine appears to have a specific action in causing the absorption of glandular swellings, and is also administered as a tonic. Iodine swallowed in the solid state causes ulceration of the mucous membrane of the stomach, and death.

Iodine is extensively used in photography. The sensitive film of the daguerreotype plate consists of iodide of silver, produced by exposing a polished plate of the metal to the action of iodine-vapour; and surfaces of paper, collodion, albumin, &c. are rendered capable of taking photographic pictures by dipping them first in a solution of nitrate of silver and then in iodide (or sometimes bromide) of potassium.

IODINE, BROMIDES OF. Iodine forms with bromine a solid, volatile, crystalline compound, probably a protobromide, IBr (Balard), and with excess of bromine, a dark brown liquid, soluble in water, probably a pentabromide, IBr^5 (Löwig). On exposing the pentabromide together with a small quantity of water to a temperature below 0°, a crystalline hydrate is formed which at + 4° is resolved into water and bromide of iodine. (Löwig.)

IODINE, CHLORIDES OF. Iodine unites directly with chlorine, forming a protochloride and a trichloride, and perhaps also a pentachloride. There is also a tetrachloride produced by decomposition of the protochloride.

Protochloride. ICl.—Of this compound there are said to be two modifications, one liquid at common temperatures, the other solid; but the differences observed are perhaps due to the presence of small quantities of foreign substances, or to slight variations in the proportions of the chlorine and iodine. It is obtained:—1. By passing dry chlorine gas over dry iodine till the whole is liquefied, but no longer.—2. By distilling iodine with chlorate of potassium, oxygen being then evolved, the protochloride distilling over, and a mixture of chloride, iodate, and perchlorate of potassium remaining behind (Berzelius):

$$I^2 + 3KClO^3 = KClO^4 + KIO^3 + KCl + O^2 + ICl.$$

The protochloride of iodine obtained by either of these processes is described as a reddish-brown oily liquid, and nothing is said about its solidification (*Gmelin's Handbook*, ii. 346). According to J. Trapp also (J. pr. Chem. lxiii. 108), the liquid protochloride obtained as above does not solidify. But P. Schützenberger (Zeitschr. Chem. Pharm. 1862, p. 1) by passing dry chlorine in the cold over dry iodine (100 grms.) till it was liquefied, then adding more iodine (50 grms.), distilling between 100° and 102°, and rectifying between the same limits, obtained a liquid which crystallised in long needles when cooled to 10° in an open vessel, but if sealed up in a flask before it had time to solidify, retained its fluidity for 24 hours even when cooled to between 2° and 3°, and when the flask was opened, solidified suddenly, with rise of temperature, like a supersaturated solution of Glauber's salt. The crystals when exposed to the air, melted at 30° and solidified again at 25°. A similar result was obtained by introducing 31 grms. of iodine into a flask containing 8·7 grms. of chlorine (quantities proportional to the atomic weights). The whole of the chlorine was rapidly absorbed, and a liquid was formed which remained unaltered for many hours at 5° or 6°, but ultimately solidified completely.—By distilling iodine with chlorate of potassium, Schützenberger likewise obtained a dark-coloured liquid which quickly crystallised.

Trapp (*loc. cit.*) has also obtained the protochloride of iodine in the solid state by strongly heating iodine in a retort till it melted, and passing a stream of dry chlorine into the iodine-vapour till all the iodine had disappeared; the upper part of the retort then became filled with a thick red-brown vapour, and the solid protochloride of iodine collected in the receiver in large, hyacinth-red, transparent prisms and tables, which melted at 25° to a red-brown oily liquid.

Protochloride of iodine is very volatile; has a pungent odour of chlorine and iodine; attacks the eyes strongly; tastes slightly acid, strongly astringent and biting; stains the skin deep-yellow, and produces smarting. It decolorises *indigo* and *litmus*, but does not give a blue colour with *starch*. It deliquesces in the air, and according to Gay-Lussac, dissolves easily in *water* without decomposition; according to Schützenberger, on the other hand, it is decomposed by water, yielding iodic and hydrochloric acids, with separation of iodine, and formation of an iodised compound, which remains dissolved in the water, but may be extracted therefrom by ether. The protochloride dissolves in *alcohol* and in *ether*, forming yellow solutions.

Protochloride of iodine sometimes decomposes spontaneously into the tetrachloride and free iodine: $4ICl = ICl^4 + I^3$ (Kämmerer, J. pr. Chem. lxxxiii. 83).—When heated, it gives off the trichloride, leaving a residue of pure iodine: $3ICl = ICl^3 + I^2$ (Kane, Phil. Mag. [3] x. 430). *Sulphurous* and *sulphydric acids* decompose it with separation of iodine. With aqueous solutions of the fixed *alkalis* it yields a chloride and iodate and free iodine:

$$6KHO + 5ICl = 5KCl + KIO^3 + 3H^2O + I^4,$$

the iodine however dissolving in excess of the alkali in the form of iodide and iodate.

—With aqueous or alcoholic *ammonia*, it yields various iodamides (the so-called iodides of nitrogen (p. 289), according to the proportions used and the manner in which the reaction takes place, *e.g.*:

$$\mathrm{3ICl + NH^3 = 3HCl + NI^3.} \quad \text{(Mitscherlich.)}$$
$$\mathrm{2ICl + NH^3 = 2HCl + NHI^2.}$$
$$\mathrm{ICl + NH^3 = HCl + NH^2I.}$$
$$\mathrm{3ICl + 2NH^3 = 3HCl + NI^3.NH^3.} \quad \text{(Bunsen.)}$$

Mercuric chloride added to a concentrated aqueous solution of protochloride of iodine throws down mercuric iodide, leaving trichloride of iodine in solution (Kane):

$$\mathrm{ICl + HgCl = HgI + ICl^3.}$$

Stannous chloride added in small quantity to the concentrated aqueous solution, precipitates iodine, and is converted into stannic chloride: but on adding a larger quantity of the stannous chloride, the iodine disappears, and stannous iodide separates in brilliant orange-coloured needles (Kane):

$$\mathrm{2ICl + SnCl^2 = I^2 + SnCl^4.}$$
$$\mathrm{2ICl + 3SnCl^2 = SnI^2 + 2SnCl^4.}$$

Protochloride of iodine acts very readily on many organic compounds, the chlorine taking up an atom of hydrogen to form hydrochloric acid, and the iodine taking its place. In this way, many iodine-substitution-compounds may be obtained which could not be formed by the action of iodine alone; *e. g.*, iodopyromeconic acid, $\mathrm{C^5H^3IO^3}$, from *pyromeconic acid*, $\mathrm{C^5H^4O^3}$ (J. Brown, Edinb. Phil. Trans. xxi. [1] 49); mono- and di-iodophenic acids, from *phenic acid*, $\mathrm{C^6H^6O}$ (Sengenwald, Compt. rend. liv. 197). On the *alcoholic hydrides*, hydride of heptyl for example, protochloride of iodine acts in a manner opposite to that just mentioned, converting them into chlorides, with elimination of hydriodic acid (Schorlemmer, p. 144). In some cases, chloride of iodine unites directly with an organic compound, with *ethylene*, for example, forming chloriodide of ethylene, $\mathrm{C^2H^4ClI}$ (Maxwell Simpson, Proc. Roy. Soc. xii. 278). According to Geuther, however (Ann. Ch. Pharm. cxxiii. 123), when dry coal-gas is passed over fused protochloride of iodine, the ethylene contained in it is converted into dichloride of ethylene:

$$\mathrm{C^2H^4 + 2ICl = C^2H^4Cl^2 + I^2.}$$

From iodised organic compounds it sometimes takes away one or more atoms of iodine, replacing them by chlorine; thus it converts *iodide of ethyl* into chloride of ethyl (Geuther):

$$\mathrm{C^2H^5I + ICl = C^2H^5Cl + I^2;}$$

di-iodide of ethylene into chloriodide of ethylene (Maxwell Simpson):

$$\mathrm{C^2H^4I^2 + ICl = C^2H^4ICl + I^2;}$$

or into dichloride of ethylene (Geuther):

$$\mathrm{C^2H^4I^2 + 2ICl = C^2H^4Cl^2 + I^4.}$$

Benzene, $\mathrm{C^6H^6}$, is violently attacked by protochloride of iodine, yielding chiefly crystalline chlorinated products of high boiling point, together with iodated bodies and free iodine.

Trichloride. $\mathrm{ICl^3}$.—This compound is produced:—1. By treating iodine at a gentle heat with excess of chlorine gas.—2. By introducing finely divided iodic anhydride into dry hydrochloric acid gas; the mass then liquefies and boils, and on cooling deposits trichloride of iodine in long needles (Serullas):

$$\mathrm{I^2O^5 + 10HCl = 2ICl^3 + 5H^2O + Cl^4.}$$

Also by mixing the crystallised iodic acid or anhydride with strong hydrochloric acid, the trichloride then crystallising out. (Soubeiran.)

Trichloride of iodine is orange-yellow, and crystallises on cooling after fusion in long needles (Serullas). It acts on other substances in the same manner as the protochloride (Kane); decolorises solution of indigo (Gay-Lussac); does not turn starch blue, except on the addition of an aqueous solution of stannous chloride, or other dechlorinating substance, which sets the iodine free.

It melts at a temperature between 20° and 25°, evolving chlorine gas, which it again absorbs on cooling (Serullas). In contact with a very small quantity of *water*, it is partly resolved into an insoluble yellowish portion (probably a mixture of trichloride of iodine and iodic anhydride), and a solution of protochloride of iodine and hydrochloric acid (Serullas):

$$\mathrm{4ICl^3 + 5H^2O = 10HCl + I^2O^5 + 2ICl.}$$

Trichloride of iodine is less readily dissolved by *water* than the protochloride; the saturated solution may be regarded either as aqueous trichloride of iodine—which is the more probable supposition; or as a mixture of hydrochloric acid and iodic acid containing free iodine; or as a mixture of hydrochloric acid and an acid of iodine which contains 2 atoms of oxygen (iodous acid):

$$5ICl^3 + 9H^2O = 15HCl + \underset{\text{Iodic acid.}}{3HIO^3} + I^2.$$

$$\text{or} \quad ICl^3 + 2H^2O = 3HCl + \underset{\text{Iodous acid.}}{HIO^2}.$$

A similar solution is obtained on passing chlorine gas to saturation, through 1 pt. of iodine diffused in 4 pts. of water, the mixture being kept cool, and the excess of chlorine afterwards removed by a current of atmospheric air. The solution, when saturated with chlorine as completely as possible, has a bright yellow colour and contains rather more than 3 atoms of chlorine to 1 atom of iodine, because the water gives rise to the formation of a small quantity of hydrochloric acid and iodic acid (Soubeiran). Solution of trichloride of iodine may also be prepared by precipitating an aqueous solution of the protochloride with mercuric chloride, and distilling the liquid after decanting it from the precipitated iodide of mercury.

When an aqueous solution of trichloride of iodine is gradually mixed with sulphuric acid, and the vessel kept cool, the trichloride separates in the form of a white curdy mass, which afterwards assumes an orange-yellow colour; on heating the mixture, it dissolves, but separates again as the liquid cools; on distilling the mixture, the trichloride passes over (Serullas). Ether does not separate trichloride of iodine from an aqueous solution (Dumas); but if protochloride of iodine is also present, the ether takes up the trichloride in company with it, provided the solution is not too dilute (Serullas). An aqueous solution of trichloride of iodine neutralised with a fixed *alkali*, yields a chloride, an iodate, and a precipitate of iodine, which redissolves in an excess of alkali in the form of iodide and iodate (Liebig):

$$5ICl^3 + 18KHO = 15KCl + 3KIO^3 + I^2 + 9H^2O.$$

On mixing the aqueous solution with an aqueous solution of neutral *iodate of potassium* and then adding alcohol, acid iodate of potassium is precipitated (Serullas). An aqueous solution of trichloride of iodine agitated with a small quantity of *oxide of silver*, yields chloride of silver and iodic acid; when a larger quantity of oxide of silver is used, the chloride of silver is mixed with iodate (Serullas), and iodide of silver is probably formed at the same time:

$$3ICl^3 + 5Ag^2O + H^2O = 9AgCl + AgI + 2HIO^3.$$

Silver-leaf is converted by aqueous trichloride of iodine into chloride and iodide of silver (Serullas). When aqueous trichloride of iodine is mixed with a small quantity of a solution of *stannous chloride*, a precipitate of iodine is obtained, soluble in excess of the tin-salt. (Kane.)

Trichloride of iodine unites with *metallic chlorides*. (Filhol.)

Tetrachloride. ICl^4.—Produced by spontaneous decomposition of the liquid protochloride, $4ICl = ICl^4 + I^3$. Crystallises in red octahedrons, the free iodine separated at the same time remaining dissolved in the mother-liquor. (Kämmerer, J. pr. Chem. lxxiii. 83.)

Pentachloride. ICl^5.—Not known in the free state. Dry iodine cannot be made to combine with 5 atoms of chlorine (Liebig). Iodine diffused in 4 pts. of water does not absorb much more than 3 atoms of chlorine, and the yellow solution obtained yields a precipitate of iodine when saturated with alkalis (Soubeiran). The same results are obtained when the quantity of water is 8 or 10 times as great as that of the iodine. If, however, the iodine be diffused through a still larger quantity of water, 20 pts. for instance (Soubeiran), the iodine combines with 5 atoms of chlorine; the solution in this case is colourless, or merely coloured yellow from excess of chlorine, which may be removed by a current of air; it exhibits all the properties of a solution of hydrochloric and iodic acids (Liebig, Soubeiran, L. Thompson):

$$I^2 + Cl^{10} + 6H^2O = 10HCl + 2HIO^3.$$

A solution of the same kind is obtained on mixing dilute hydrochloric and iodic acids. It smells strongly of chlorine and slowly decolorises a solution of indigo (Gay-Lussac). Strong sulphuric acid precipitates trichloride of iodine from it and liberates chlorine. (Soubeiran.)

IODINE, DETECTION AND ESTIMATION OF. Iodine in the free state is easily recognised by the violet vapour which it gives off when heated, and by its reaction with starch. The starch for this purpose should be perfectly colourless; it may be prepared by boiling potato-starch or arrow-root with water and leaving it to cool. To obtain a delicate reagent, Béchamp (Zeitschr. Analyt. Chem. i. 466), recommends the following mode of preparation. Gelatinous starch is boiled with a quantity of concentrated potash-ley equal to $\frac{1}{10}$ of the weight of the dry starch contained in it, till it has become perfectly fluid; the liquid is then diluted with water, supersaturated with acetic acid, and precipitated with alcohol; and the bulky precipitate is boiled first with alcohol of 60 vol. per cent. then washed, first with alcohol acidulated with sulphuric acid, then with pure alcohol of the same strength, and dried. For use, the dried preparation is to be suspended in hot water.

When iodine exists in solution in the form of hydriodic acid or a metallic iodide, it may be separated by the addition of chlorine-water, sulphuric acid, or nitric acid, and will then give the blue colour with starch. When chlorine-water is used, care must be taken not to add an excess, as a chloride of iodine will then be formed which will not exhibit the starch reaction. (See IODIDES, p. 287.)

The methods of detecting iodine in insoluble iodides, and in presence of oxygen, sulphur, phosphorus, &c., are the same as those employed when it is to be estimated quantitatively.

Quantitative Estimation.—Iodine in the free state is best determined by means of a standard solution of sulphurous acid (see ANALYSIS, VOLUMETRIC, i. 265). When it occurs in the solution in the form of hydriodic acid or a metallic iodide, it may either be set free by *chlorine-water* and estimated volumetrically in the same manner; or it may be precipitated by *nitrate of silver* in the same manner as chlorine and bromine (i. 677, 903). 100 pts. of iodide of silver correspond to 54·128 pts. of iodine.

It may also be precipitated as iodide of palladium, by mixing the solution with chloride or *nitrate of palladium.* A black precipitate then falls, which settles down slowly but completely, and when ignited, leaves metallic palladium, 100 pts. of which are equivalent to 239·62 pts. of iodine.

This last method of precipitation serves also to separate iodine from bromine and chlorine. If the chlorine is also to be estimated, the precipitation must of course be made with nitrate of palladium, not with chloride. If bromine is present without chlorine, the iodine must be precipitated with chloride of palladium, because the nitrate would precipitate bromine as well as iodine; the precipitation of the bromine may however be prevented by the addition of a soluble chloride. To estimate the chlorine and bromine in the filtered liquid, the excess of palladium is removed by sulphydric acid and the excess of the latter by means of nitric acid or a ferric salt. The bromine and chlorine may then be precipitated by nitrate of silver, and the precipitate treated in the manner already described (i, 903). Iodine may also be estimated in presence of chlorine by the method already described (i. 678) for the estimation of bromine, viz., by precipitating the two elements with nitrate of silver and heating the silver precipitate in a stream of chlorine. The quantity of iodine is equal to the loss of weight multiplied by $\frac{127}{127 - 35\cdot5} = 1\cdot28$.

A precisely similar method may be applied to the determination of iodine in presence of bromine, the precipitate of iodide and bromide of silver being ignited in bromine-vapour, and the loss of weight multiplied by $\frac{127}{127 - 80} = 2\cdot70$.

For other methods of estimating iodine in presence of chlorine and bromine, see i. 678.

The method of decomposing *insoluble iodides*, so as to obtain the iodine in solution, are similar to those adopted for insoluble bromides (i. 678).

Iodates and *periodates* are reduced to iodides by the action of sulphurous or sulphydric acid. To decompose them by ignition would not give accurate results, as a portion of the iodine would be driven off.

The compounds of iodine with *phosphorus*, *arsenic* and *antimony* may be decomposed and analysed by treating them with water or aqueous alkalis, whereby the iodine is converted into hydriodic acid, and may then be precipitated with nitrate of silver from a solution acidulated with nitric acid. The iodides of *sulphur* are most readily analysed by heating them in a combustion-tube with nitrate of potassium and carbonate of sodium, whereby the iodine and sulphur are converted into metallic iodide and sulphate. (Guthrie, Chem. Soc. J. xiv. 59.)

Iodine in *organic compounds* may be estimated in the same manner as chlorine (i. 247). In the more easily decomposible compounds, such as the iodated organic acids, the iodine may also be determined by decomposing the compound with water and sodium-amalgam, then acidulating the solution with nitric acid, and precipitating with nitrate of silver. The same method may be applied to the corresponding bromine- and chlorine-compounds. (Kekulé, Ann. Ch. Pharm. Suppl. i. 338.)

Atomic Weight of Iodine.—The earlier attempts to determine the atomic weight of this element, by Proust, Davy, Gay-Lussac and Berzelius, gave results varying from 84 to 126, that is to say, considerably below those obtained by more recent determinations. Millon, by igniting iodate of potassium and iodate of silver, and weighing the remaining iodides, obtained the number 126·47; but the result is not quite exact, because the iodides themselves are partly decomposed by ignition.

The most exact determinations have been made by **Marignac** (Bibl. univ. de Genève, xlvi. 367) and **Dumas** (Ann. Ch. Pharm. cv. 93). Marignac determined the quantity of iodide of potassium required for precipitating a known quantity of silver from the nitrate, and found, as the mean of five closely agreeing experiments, that 100 pts. silver are precipitated from the solution of the nitrate by 153·74 pts. iodide of potassium; whence the proportion $100 : 153\cdot74 = 108 : x$ gives 166·04 for the atomic weight of iodide of potassium; and this diminished by 39·2, the atomic weight of potassium, gives for that of iodine the number 126·84.

In another set of experiments, Marignac determined the quantity of iodide of silver precipitated by iodide of potassium from a known weight of silver dissolved in nitric acid. As the mean of three closely agreeing experiments, he found that 100 pts. of silver give 217·511 pts. AgI: hence the atomic weight of iodide of silver is $\frac{217\cdot511 \times 108}{100} = 234\cdot91$, which, diminished by 108, gives for iodine the number 126·91.

Dumas decomposed pure iodide of silver by ignition in a stream of chlorine, and weighed the chloride of silver thus produced. In one experiment 3·520 grms. iodide of silver gave 2·149 chloride; in another 7·011 iodide gave 4·281 chloride. Both these results give for iodine the atomic weight 127, which is the number now adopted.

IODINE, OXIDES AND OXYGEN-ACIDS OF. The series of oxidised compounds of iodine is not as yet so complete as that of chlorine. The following have been described and analysed with more or less accuracy:

Acids.		*Oxides or Anhydrides.*	
Hypo-iodous acid . . .	HIO		
		Millon's Sub-hypo-iodic acid . .	$I^{10}O^{19}$
		Periodic oxide (Millon's Hypo-iodic acid)	IO^2 or I^2O^4
		Intermediate Iodic oxide . .	I^8O^{18}
Iodic acid	HIO^3	Iodic anhydride	I^2O^5
Periodic acid	HIO^4	Periodic anhydride . . .	I^2O^7.

Of these, the only compounds whose composition has been established with certainty are iodic and periodic acids, with their corresponding anhydrides and salts. The existence of hypo-iodous acid and of periodic oxide has been rendered probable by experiments which will be presently described. The remaining oxides, $I^{10}O^{19}$ and I^8O^{18}, are of very doubtful constitution: the substances analysed were perhaps impure periodic oxide, or the last may have been iodic anhydride containing excess of iodine.

Hypo-iodous acid. HIO?

An oxygen-acid of iodine corresponding to hypochlorous acid appears to exist, but neither the acid nor its salts have yet been obtained in definite form. According to Magnus and Ammermüller, disodic periodate gives off part of its oxygen when ignited, and yields a residue, the solution of which in cold water possesses bleaching properties (p. 310). **Mitscherlich** (Pogg. Ann. xi. 162; xvii. 481), by dissolving iodine in moderately strong soda-ley, till the liquid began to show colour, and evaporating at a low temperature, obtained a salt consisting of $Na^2I^2O^3.\ 10H^2O$, which however might have been a mixture composed of iodide and iodate of sodium: $NaI.NaIO^3\ 10H^2O$; in fact the salt when treated with alcohol is resolved into soluble iodide and insoluble iodate. **Wöhler** (Pogg. Ann. viii. 96), by distilling iodine with anhydrous peroxide of barium, obtained a yellow liquid which he regarded as hypo-iodous acid, or rather, anhydride. (Vid. Gm. ii. 252.)

According to **Schönbein** (J. pr. Chem. lxxxiv. 385), when 1 at. iodine is dissolved in an aqueous solution of 1 at. potash, the formation of iodate of potassium does not take place immediately, but is preceded by that of hypo-iodite of potassium, just as in the case of chlorine; the solution, which has the odour of saffron, and exhibits properties similar to those of the hypochlorites, is however very unstable, the hypo-iodite being resolved, gradually at ordinary temperatures, and instantly at the boiling heat, into iodide and iodate: $3KIO = 2KI + KIO^3$. Schönbein also finds that hypo-iodite of ammonium is formed by the action of iodine on excess of ammonia.

According to **Lenssen** and **Löwenthal** (J. pr. Chem. lxxxvi. 216), hypo-iodous acid is contained in the solution formed by the action of carbonate of sodium (or other alkaline liquid) on trichloride of iodine, which is yellow, reddens benzene, colours starch blue, and contains a salt having the composition NaI^3O or $NaIO.I^2$, that is, hypo-iodite of sodium with 2 atoms of free iodine, on the removal of which, either by excess of alkali, sulphurous acid, benzene, or other reagents, the hypo-iodite of potassium is immediately resolved into iodide and iodate. The alkaline solution of hypo-iodous acid is decomposed by iodide of potassium, yielding free alkali and free iodine, according to the equation:

$$KI + NaIO + H^2O = KHO + NaHO + I^2.$$

The subject requires further examination.

Periodic oxide, IO^2, *and Oxides nearly allied to it in composition.*

Periodic oxide is obtained, according to Millon, by treating with dilute alcohol the powder (p. 299) produced by the action of fuming nitric acid on iodine, regarded by Kämmerer as nitroso-iodic anhydride, $I^2O^4(NO)^2$.

When iodic anhydride is heated with 5 pts. of strong sulphuric acid, till a few bubbles of oxygen are given off, a scaly sulphur-yellow substance is formed, which appears to consist of $4I^2O^5.2IO^2.SO^4H^2$. If the boiling be continued, the evolution of oxygen goes on, and crystals are formed, having a much deeper yellow colour than the preceding, and apparently consisting of $2I^2O^5.IO^2.SO^3H$. Water decomposes both these compounds into sulphuric acid, iodic acid, and iodine. By continuing the action of the sulphuric acid till iodine begins to escape as well as oxygen, two other compounds are formed, to which Millon assigns the formulæ $2IO^2.2SO^3.H^2O$ and $I^{10}O^{19}.10SO^3.H^2O$. These substances, subjected to the action of moist air, appear to yield the compounds IO^2 and $I^{10}O^{19}$ in the free state. To the latter, Millon gives the name *sub-hypo-iodic acid* [*anhydride*].

When sulphurous anhydride is allowed to act upon iodic anhydride longer than is required to form the compound $5I^2O^5.SO^3$ (p. 299), a large quantity of iodine is separated, and a lumpy adhesive mass is formed, which, if left for a day standing over water in a bell-jar, then washed with alcohol and with water, leaves an oxide of iodine containing I^6O^{13}, contaminated with a small quantity of sulphuric acid. It is a brown-yellow powder which does not decompose in the air, but absorbs a small quantity of water from it. Dilute nitric acid dissolves it, with separation of iodine; fuming nitric acid converts it into iodic acid. When heated to 100°, it splits up into iodine and iodic anhydride: $5I^6O^{13} = 13I^2O^5 + I^4$. Water decomposes it slowly at ordinary temperatures, quickly at 100°, into iodine and iodic acid.

Aqueous alkalis act in the same manner; but alcoholic alkalis do not act upon it at ordinary temperatures. This circumstance distinguishes it from the oxides IO^2 and $I^{10}O^{19}$ above-mentioned, which, according to Millon, form with alcoholic potash, brick-red easily decomposible salts. Absolute alcohol, ether, acetic ether, and sulphide of carbon are likewise without action on the oxide I^6O^{13}, even at the boiling heat. (Kämmerer, J. pr. Chem. lxxxiii. 72.)

Iodic acid, Anhydride and Salts.

Iodic Acid. HIO^3. (Gm. ii. 253.)—This acid is produced by the action of oxidising agents upon iodine in presence of water or alkalis. According to Pettenkofer (Jahresber. 1857, p. 581), it is sometimes found in commercial nitric acid (the iodine being doubtless derived from the Chili saltpetre used in the preparation). According to Riche (Compt. rend. xlvi. 348), it is produced by the electrolysis of aqueous hydriodic acid or aqueous iodine; in the former case, the hydriodic acid is simply oxidised to HIO^3 by oxygen evolved by the decomposition of the water; in the latter the iodine is first converted into hydriodic acid, which is then oxidised in the manner just mentioned. It is also produced by the action of iodine on chloric or bromic acid. (Kämmerer, J. pr. Chem. lxxxv. 452.)

Preparation.—1. Small quantities of iodic acid are conveniently prepared by heating iodine with the strongest nitric acid free from nitrous acid in a wide glass tube, and leaving the liquid to cool. Iodic acid is then deposited in crystals (Connel). Jacquelain (Ann. Ch. Phys. [3] xxx. 332) recommends this as the best mode of preparing iodic acid in all cases. He heats 5 grms. of dry iodine in a flask with 200 grms. nitric acid of specific gravity 1·5 to 60° for an hour; decants the supernatant liquids (the upper consisting of nitric acid containing pernitric oxide, the lower of a red-brown solution of iodine in nitric acid) from the separated iodic acid; distils these liquids down to one-sixth; and gently heats the residue, together with the crystallised iodic acid, in a vessel in which it is protected from dust; iodic anhydride then separates in nacreous crystals.—2. For preparing larger quantities, Liebig's method is, however, generally preferred. It consists in suspending an ounce or two of pulverised iodine in a pound of water, and passing a stream of chlorine through the liquid, till the iodine is completely dissolved:

$$6H^2O + 5Cl^2 + I^2 = 10HCl + 2HIO^3.$$

The brown strongly acid liquid is then slightly supersaturated with carbonate of sodium, whereby a considerable quantity of iodine is precipitated, which may be collected on a filter, then suspended in water, and treated with chlorine as before. The filtered solution contains iodate and chloride of sodium, with a trace of carbonate, which may be neutralised by hydrochloric acid. On afterwards adding chloride of barium to the filtered liquid as long as a precipitate is formed, the whole of the iodic acid is thrown down as iodate of barium, which may be collected on a filter, dried, and then decomposed by boiling it for half an hour with 2 pts. of oil of vitriol diluted with 10 or 12 pts. of water. The iodic acid thus liberated dissolves in the water, and the solution filtered from the sulphate of barium and evaporated at a gentle heat, yields the acid in the form of a crystalline mass. Kämmerer (J. pr. Chem. lxxix. 94) dissolves iodine in hot saturated baryta-water; filters the solution of iodide of barium from the separated iodate; passes chlorine through the filtrate (which at first precipitates iodine, but in a state of very fine division, so that it is very quickly oxidised), and thereby converts the whole of the iodide of barium into iodate, from which the iodic acid may then be separated by sulphuric acid.—3. Another very good method of preparing the acid is to digest 4 pts. of iodine with 7·5 pts. of chlorate of potassium in 40 pts. of water acidulated with 10 pts. of nitric acid, and heat the liquid sufficiently to cause rapid evolution of chlorine. In a short time the iodine is completely oxidised, and the iodic acid thus formed may be precipitated by baryta, and separated again by sulphuric acid. The largest crystals are obtained when the solution contains a slight excess of sulphuric acid.

The crystallised acid, HIO^3 or $I^2O^5.H^2O$, when exposed to a heat of 130°, or digested in absolute alcohol, is partly resolved into water and iodic anhydride, which remains combined with the iodic acid, forming the compound $I^2O^5.HIO^3$ or $3I^2O^5.H^2O$:

$$3HIO^3 = I^2O^5.HIO^3 + H^2O,$$

which at 170° suffers further decomposition, yielding water and iodic anhydride.

Iodic anhydride, I^2O^5, crystallises in forms belonging to the trimetric system, and often reduced to the tabular form by the predominance of two parallel faces ∞P. For P the ratio of the principal to the secondary axes is 1 : 0·7586 : 0·7122. Angles P : P in the terminal edges = 99° 22′, and 105° 12′; in the lateral edges = 125° 7′; $\infty P : \infty P$ = 93° 37′. The pyramidal faces occur sphenoïdo-hemihedrally. Cleavage perfect parallel to $\breve{P}\infty$; imperfect parallel to $\bar{P}\infty$ (Schabus, *Bestimmung der Krystallgestalten in chemischen Laboratorien erzeugter Produkte*, Wien, 1855; Jahresber. 1854, p. 310). Specific gravity of the crystals = 4·250 (Filhol, Ann. Ch. Phys. [3] xi. 415). At the temperature of boiling olive-oil, the anhydride is completely resolved into iodine and oxygen. It dissolves in water, forming iodic acid.

Pulverised iodic anhydride is reduced at ordinary temperatures by a small quantity of *sulphurous anhydride*, yielding sulphuric anhydride and free iodine; by continued action of sulphurous anhydride at 100°, it is converted into a light yellow granulo-crystalline mass, consisting of an **iodosulphuric anhydride**, $5I^2O^5.SO^3$. This compound is quickly decomposed by contact with air and water, with separation of iodine. By absolute alcohol or ether, it is resolved into I^2O^5 and SO^3; and by alcoholic potash it is converted into iodate and sulphate of potassium. Strong sulphuric acid does not act upon it at common temperatures; hydrochloric acid dissolves it, with evolution of chlorine and formation of chloride of iodine. By still longer exposure to the action of sulphurous anhydride, the iodic anhydride is completely decomposed, yielding a large quantity of iodine, and an adhesive mass containing an oxide of iodine, I^8O^{19} (p. 298).

Nitro-iodic anhydride, $I^2O^4(NO)^2$?—Millon (Ann. Ch. Phys. [3] xii. 330), by triturating iodine with strong nitric acid, obtained a yellow powder which he regarded as a compound of nitric acid with periodic oxide, IO^2; it was resolved by water into nitric acid, iodic acid, and iodine, and when treated with dilute alcohol yielded a small quantity of periodic oxide, IO^2 (Millon's *hypo-iodic acid*). Kämmerer (J. pr. Chem. lxxxiii. 72) has obtained the same substance by Millon's method, also by treating iodine with a mixture of fuming nitric and strong sulphuric acids, and assigns to it the composition above given. He finds that it is decomposed by drying over lime, with evolution of nitric oxide, and that, when dried in an atmosphere of carbonic anhydride, it splits up into nitric oxide and periodic oxide. It is decomposed by water and by aqueous acids and alkalis; hydrochloric acid dissolves it, with evolution of chlorine and formation of chloride of iodine. Alcohol, ether, and acetic ether are violently attacked, often with incandescence, even by small quantities of the compound. By exposure to moist air at common temperatures, it is decomposed into iodine, iodic acid, and nitric acid; in dry and very cold air it remains unaltered for a long time. It dissolves slowly, and without decomposition, in strong sulphuric acid, and sometimes separates from the solution spontaneously, but is easily precipitated on scratching the sides of the vessel with a glass rod, or adding fuming nitric acid to the solution. The sulphuric acid solution, when boiled, gives off a large quantity of nitric oxide.

Iodic acid, HIO^3, crystallises from a strong aqueous solution in transparent six-sided tables without water of crystallisation (Serullas, Marignac). According to Rammelsberg (Pogg. Ann. xc. 12) the crystals are trimetric, the ratio of the brachydiagonal, macrodiagonal, and principal axis being = 0·58905 : 1 : 1·1903. They exhibit the faces ∞P, $\bar{P}\infty$, oP, with $\frac{1}{2}\breve{P}\infty$ and $2\breve{P}\infty$ subordinate. In the brachydiagonal principal section $\infty P : \infty P = 119° 0'$; $\breve{P}\infty : \breve{P}\infty = 80° 4'$. The crystals are transparent and have a vitreous lustre; they are generally either tabular by predominance of oP, or elongated in the direction of the brachydiagonal; cleavage distinct parallel to oP, less distinct parallel to ∞P. According to Marignac (Jahresber. 1856, p. 296, 1857, p. 124) iodic acid crystallises from aqueous solution at 50°—60° for the most part in the form determined by Schabus for the anhydride,* less abundantly in the form just described as determined by Rammelsberg. Marignac finds, however, different values for some of the angles, viz., $\infty P : \infty P$ in the brachydiagonal principal section $= 114° 46'$; $\breve{P}\infty : \breve{P}\infty$ in the same $= 79° 38'$. Kämmerer (J. pr. Chem. lxxxv. 452) has obtained a hydrate of iodic acid, $2HIO^3.9H^2O$, which crystallises at 17° in beautiful hexagonal tables.

Iodic acid is very soluble in *water*, slightly soluble in *alcohol*. The aqueous acid bleaches litmus paper after first reddening it. It is easily decomposed by *deoxidising agents*, yielding in the first instance hydriodic acid, which then, with the remaining iodic acid, forms water and free iodine:

$$HIO^3 + 5HI = 3H^2O + I^6.$$

Hence aqueous iodic acid, though it does not of itself impart a blue colour to starch, produces this colour immediately on the addition of hydriodic, sulphydric or sulphurous acid, stannous chloride, vegetable acids, or other deoxidising agents. In some cases however an excess of the reducing agent converts the free iodine into hydriodic acid and destroys the blue colour: thus with sulphurous acid:

$$\underset{\text{Sulphurous acid.}}{H^2SO^3} + I^2 + H^2O = 2HI + \underset{\text{Sulphuric acid.}}{H^2SO^4}.$$

Nitric oxide gas reduces aqueous iodic acid at ordinary temperatures (Kämmerer). The acid heated in sealed tubes with *sulphide of carbon* is reduced to hydriodic acid; in like manner iodate of potassium to iodide (Schlagdenhauffen, J. Pharm [3] xxxiv. 175). *Ferrous sulphate* does not of itself appear to reduce iodic acid, but on addition of caustic soda and subsequent supersaturation with sulphuric acid, iodine is set free. In this case, it may be supposed that the ferrous sulphate first separates iodine, which is taken up by the soda-ley, forming iodide and iodate of sodium, and that, on addition of sulphuric acid, iodic and hydriodic acids are set free, which act upon each other in the way above mentioned, yielding free iodine (Hempel, Ann. Ch. Pharm. cvii. 97). Aqueous iodic acid yields by *electrolysis*, oxygen at the positive, and iodine at the negative pole, the separation of the latter being due to the action of nascent hydrogen resulting from the decomposition of the water. According to Buff (Ann. Ch. Pharm. cx. 257), the iodic acid is resolved by the current into H and IO^3, which latter is decomposed by the water, yielding HIO^3 and free oxygen.

Iodates. Iodic acid is monobasic, like chloric and bromic acids, the general formula of its normal salts being

$$MIO^3 = \left.\begin{matrix} IO^2 \\ M \end{matrix}\right\} O \text{ or } M^2O.I^2O^5.$$

But there are likewise acid iodates, or more properly anhydro-iodates, which may be regarded as compounds of the normal iodates with one or more molecules of iodic anhydride: thus there are three iodates of potassium, having the following formulæ:

Normal iodate of potassium	$2KIO^3$ or $K^2O.I^2O^5$.
Di-iodate of potassium . . .	$2KIO^3.I^2O^5$ or $K^2O.2I^2O^5$.
Tri-iodate of potassium . . .	$2KIO^3.2I^2O^5$ or $K^2O.3^2IO^5$.

The normal iodates are obtained: 1. By bringing iodine in contact with an alkali and water, and removing the metallic iodide formed at the same time, by digestion in alcohol.—2. By direct mixture of iodic acid with a salifiable base.—3. By bringing the aqueous acid in contact with metals.

Most iodates are insoluble or sparingly soluble in water, the only easily soluble iodates being the ammonium-, potassium-, and sodium-salts. The solutions of these salts give with somewhat concentrated solutions of strontium- and calcium-salts, and with dilute solutions of barium-, lead-, and silver-salts, white crystalline, granular precipitates. The silver-precipitate is easily soluble in ammonia, very slightly soluble in nitric acid.

The normal iodates, when heated, either give up 3 atoms of oxygen, but no iodine, and are converted into metallic iodides (*e. g.* $KIO^3 - O^3 = KI$), or they part with their iodine and 5 atoms of oxygen, and are reduced to metallic oxides (*e. g.* $Ba^2O.I^2O^5 - O^5 - I^2 = Ba^2O$), accordingly as the metal has greater affinity for iodine or for oxygen. Some iodates detonate when heated with combustible bodies, *e. g.* on red-hot coals,—sometimes even when merely struck; but the detonation is much weaker than that produced by chlorates or nitrates. The aqueous solution of an iodate mixed with sulphurous acid yields iodine and sulphuric acid, part of which combines with the base (Gay-Lussac.) With sulphydric acid, the solution of an iodate yields hydriodic acid, water, sulphur, and a sulphate (H. Rose); with hydriodic acid, or with a dissolved iodide mixed with an acid to liberate the hydriodic acid, its yields a metallic iodide, iodine, and water:

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* The crystals examined by Schabus probably consisted of the acid, not of the anhydride.

$$KIO^3 + 6HI = KI + I^6 + 3H^2O.$$

Iodides and iodates containing weak bases may also decompose one another in solution without the intervention of an acid, yielding an oxide and free iodine: thus with the zinc-salts:

$$ZnIO^3 + 5ZnI = 3Zn^2O + I^6.$$

With hydrochloric acid, the iodates form water, a metallic chloride, trichloride of iodine, and free chlorine; and the metallic chloride thus produced often enters into combination with the trichloride of iodine (Filhol):

$$KIO^3 + 6HCl = 3H^2O + KCl + ICl^3 + Cl^2.$$

Arsenious acid, with the aid of heat, and likewise dichloride of tin, separate iodine from aqueous solutions of the iodates (Simon). Dilute sulphuric acid at a boiling heat separates the iodic acid from these salts (Gay-Lussac). When an aqueous solution of an iodate is heated with nitric acid, that acid at first takes hold of the base, either wholly or in part; but when the solution is evaporated to dryness and more strongly heated, the less volatile iodic acid drives out the nitric acid. (Penny, Ann. Pharm. xxxvii. 203.)

Iodates heated with strong hydrochloric acid and mercury, or with strong sulphuric acid and ferroso-ferric oxide, impart a blue colour to starch, in consequence of the liberation of iodine.

Iodate of Aluminium. A solution of moist hydrate of alumina in iodic acid evaporated to a syrup and then left over sulphuric acid, yields deliquescent crystals.

Iodate of Ammonium, $(NH^4)IO^3$, is produced by saturating caustic ammonia or carbonate of ammonium with iodic acid or chloride of iodine, and separates as a crystalline powder if the solutions are moderately concentrated. By spontaneous evaporation it is generally said to be obtained in small shining cubes. According to Marignac, however (Ann. Min. [5] ix. 1), the crystals are dimetric, exhibiting the combination oP . ∞P∞, often with P, 2P, ∞P, P∞ and 2P∞ subordinate. Angle oP : P = 124° 54; oP : 2P = 105° 14′; oP : P∞ = 134° 37; P : P in the terminal edges = 109·7°. That the crystals are not monometric, is also shown by the observation of Marbach (Jahresber. 1855, p. 145), that they act upon polarised light. It decomposes with a hissing noise at 150°, giving off equal volumes of oxygen and nitrogen together with iodine and water. It detonates on glowing coals, and is decomposed by hydrochloric acid, yielding a compound of sal-ammoniac and trichloride of iodine, together with water and free chlorine (Filhol). It dissolves in 38·5 pts. of cold water at 15°, and in 6·9 pts. of boiling water. (Rammelsberg.)

Iodate of Barium, $2BaIO^3.H^2O$.—This salt is precipitated when iodine is dissolved in baryta-water, iodide of barium remaining in solution. It may also be prepared by saturating an aqueous solution of trichloride of iodine with carbonate of barium or baryta-water, or by precipitating a concentrated solution of chloride of barium with iodate of sodium. The hydrated salt forms a granular powder. From a solution in hot nitric acid, however, it is deposited on cooling or on addition of ammonia, in small crystals (Rammelsberg), which, according to Marignac (*loc. cit.*) are monoclinic and isomorphous with bromate and chlorate of barium, exhibiting the combination ∞P . (P∞) . − P∞. Angle ∞P : ∞P in the clinodiagonal principal section = 82° 0′; (P∞) : (P∞), in the same = 76° 42′; − P∞ : ∞P = 119° 4′. The water of crystallisation escapes at a temperature below 200°. On heating the salt more strongly in a porcelain retort, vapour of iodine and oxygen gas are evolved, and a residue is obtained, consisting of basic periodate of barium (Rammelsberg):

$$5BaIO^3 = BaIO^4.2Ba^2O + 4I + O^9.$$

It does not detonate on ignited charcoal, but sometimes exhibits phosphorescence (Gay-Lussac). Hydrochloric acid dissolves it readily, even in the cold, the liquid assuming a dark-yellow colour (probably arising from the formation of a double chloride of iodine and barium) and evolving chlorine. It dissolves with difficulty in warm nitric acid (Rammelsberg). It is soluble in 3,333 pts. of water at 18°, in 625 pts.

of boiling water (Gay-Lussac), in 1,746 pts. of water at 15°, and in 600 pts. of boiling water (Rammelsberg); the anhydrous salt dissolves in 3,018 pts. water at 13·5°, and in 661 pts. boiling water. (Kremers, Pogg. Ann. xciv. 255.)

Iodate of Bismuth, $2\overset{'''}{\mathrm{Bi}}\mathrm{I^3O^9.H^2O}$.—Iodate of sodium added in excess to a solution of bismuth which is no longer precipitated by water, throws down the whole of the bismuth as iodate. The precipitate is nearly insoluble in nitric acid. When ignited it leaves trioxide of bismuth mixed with iodide.

Iodate of Calcium, $\mathrm{2CaIO^3.5H^2O}$.—Crystallises slowly from the mixed solutions of iodate of potassium and chloride of calcium in water (Pleischl), a large proportion of the salt, however, remaining dissolved (Rammelsberg). The crystals are rendered anhydrous by heat. The dry salt gently ignited in a porcelain retort evolves 14·785 per cent. of oxygen and 54·072 of iodine, leaving a residue amounting to 31·143 per cent., and consisting chiefly of pentabasic periodate of calcium; but when heated more strongly, it evolves a still larger amount of oxygen (in the whole 17·176 per cent.) and of iodine (in the whole 62·478 per cent.), and leaves 20·346 per cent. of a mixture of pentabasic periodate and much free lime, which may be separated by water (Rammelsberg, Pogg. Ann. xliv. 576). Iodate of calcium detonates violently on ignited charcoal (Gay-Lussac). When treated with concentrated hydrochloric acid, by which it is readily dissolved, it yields an orange-coloured liquid, smelling of trichloride of iodine, and similar to that yielded by iodate of potassium; it does not, however, give crystals of the double chloride of iodine and calcium (Filhol). The hydrated salt forms four-sided prisms, which effloresce in the air, with partial loss of water, and become anhydrous at a temperature below 200° (Rammelsberg). From a solution acidulated with nitric acid, it separates in trimetric crystals, $\infty P \,.\, \infty\breve{P}\infty \,.\, 3P \,.\, P \,.\, oP \,.\, 3\breve{P}\infty \,.\, 4\breve{P}\infty$. Ratio of axes, $a : b : c = 0{\cdot}4537 : 1 : 0{\cdot}5231$. $\infty P : \infty P$ in the brachydiagonal $= 132° 55'$; $oP : P = 127° 22'$; $oP : 3P = 104° 17'$ (Senarmont, Marignac, Jahresber. 1857, p. 125). The crystals dissolve in 454 pts. of water at 18°, and in 102 pts. of boiling water (Gay-Lussac); in 253 pts. at 15°, in 75 pts. of boiling water, and much more copiously in nitric acid. From the latter solution the salt is precipitated by ammonia in prisms (Rammelsberg). Alcohol separates the salt from an aqueous solution. (O. Henry.)

Iodate of Cerium, $\mathrm{2CeIO^3.H^2O}$, is a white precipitate which gives off its water at 200°, and leaves pure ceric oxide when ignited.

Iodate of Cobalt, $\mathrm{2CoIO^3.H^2O}$, is obtained by dissolving recently precipitated carbonate of cobalt in hot aqueous iodic acid, and separates partly on cooling, partly by evaporation, in violet-red crystalline crusts. Dissolves in 148 pts. of cold and 90 pts. of hot water. Gives off its water of crystallisation at 200°. At a red heat, it gives off iodine and oxygen and leaves cobaltoso-cobaltic oxide, $\mathrm{Co^3O^4}$. Alcohol added to a solution of this salt in sal-ammoniac, throws down a pale-red double salt.

Iodate of Copper.—Iodate of sodium forms with sulphate of copper (after some time only if the solutions are dilute) a greenish-blue precipitate, consisting of $\mathrm{4CuIO^3.3H^2O}$, which gives off its water at 200° (Rammelsberg). According to Millon, iodic acid forms, even in very dilute solutions of copper-salts, a blue crystalline precipitate composed of $\mathrm{2CuIO^3.H^2O}$, and the same compound is obtained by digesting recently precipitated hydrate or carbonate of copper with iodic acid at ordinary temperatures. When hydrated cupric oxide is washed with boiling water and covered with a sufficient quantity of solution of iodic acid, an olive-coloured powder is obtained which has the same composition as the blue crystals, but requires a temperature about 40° higher to dehydrate it completely. Ignited cupric oxide shaken up with aqueous iodic acid, forms a basic salt, $\mathrm{3(2CuIO^3.Cu^2O).H^2O}$, which however is converted into the olive-coloured salt when the mixture is boiled.

Iodates of Iron.—*Ferric Iodate*, $\mathrm{Fe^4O^3.2I^2O^5.8H^2O}$ or $4\mathit{fe}\mathrm{IO^3}.\mathit{fe}^2\mathrm{O.8H^2O}$, is a yellowish-white precipitate obtained by adding iodate of sodium to ammonio-ferric sulphate. The precipitate when dry becomes heavier and assumes a reddish tint. It is soluble in nitric acid, and leaves pure ferric oxide when ignited.

Ferrous Iodate is produced on mixing ferrous sulphate with iodate of potassium, as a white precipitate, which dissolves readily in excess of the ferrous sulphate, but quickly turns brown and decomposes, with evolution of iodine, especially when heated. The brown precipitate dissolves in hydrochloric acid, with evolution of chlorine, and ammonia throws down from the solution a mixture of ferric hydrate and iodide of nitrogen.

Iodate of Lanthanum, $\mathrm{2LaIO^3.H^2O}$.—Precipitated as a crystalline powder on adding sulphate of lanthanum to aqueous iodic acid. From solution in hot water, it separates on evaporation in white crystalline scales. Gives off its water at a temperature above 110°. (Holzmann, J. pr. Chem. lxxv. 321; Hermann, *ibid.* lxxxii. 385.)

Iodate of Lead, $\mathrm{PbIO^3}$.—White precipitate, very sparingly soluble in water and in nitric acid. Gives off iodine and oxygen when heated, and leaves a mixture of oxide and iodide of lead, from which the oxide is easily dissolved out by acetic acid.

Iodate of Lithium, $LiIO^3$.—Crystalline crusts, soluble in 2 pts. of water.

Iodate of Magnesium, $MgIO^3.2H^2O$.—Shining crystals soluble in 3 pts. of boiling and 9·43 pts. of cold water. They are monoclinic, exhibiting the combination, $\infty P\ .\ \infty P\infty\ .\ +P\ .\ -P\ .\ oP\ .\ -\frac{1}{2}P\infty$. In the clinodiagonal principal section, $\infty P : \infty P = 78° 20'$; $+P : +P = 91° 53'$; $-P : -P = 120° 30'$; further, $oP : \infty P\infty = 100° 40'$; $oP : -\frac{1}{2}P\infty = 155° 32'$. The crystals cleave very distinctly parallel to $\infty P\infty$ (Marignac, Jahresber. 1857, p. 125). When heated they quickly become opaque and give off water, becoming completely anhydrous at 240° (Millon). At a red heat, the salt suffers decomposition and leaves pure magnesia.

Iodate of Manganese, $MnIO^3$, is best obtained by precipitating a concentrated solution of acetate of manganese with iodate of sodium. It is pale red, soluble in 200 pts. of water, and when ignited leaves pure manganoso-manganic oxide. According to Berzelius, it contains ½ at. water ($2MnIO^3.H^2O$).

Iodates of Mercury.—1. *Mercuric Iodate.* Produced by digesting recently precipitated mercuric oxide in iodic acid. It is a white anhydrous powder, insoluble in water, but dissolving easily in hydrochloric acid, with evolution of chlorine. The solution mixed with stannous chloride yields a red precipitate of mercuric iodide, which by the further action of the tin-salt is reduced to yellow mercuroso-mercuric iodide. Mercuric iodate when heated gives off oxygen and is converted into iodide.

2. *Mercurous Iodate*, $HhgIO^3$.—A solution of mercurous nitrate rendered as neutral as possible, yields with iodate of sodium a white precipitate, which is dissolved by hydrochloric acid, with evolution of chlorine, and yields a solution from which ammonia throws down iodide of nitrogen. It dissolves with difficulty in nitric acid, and is completely volatilised by heat, being at the same time resolved into mercuric iodide, mercury and oxygen.

Iodate of Nickel, $2NiIO^3.H^2O$.—Obtained by dissolving recently precipitated hydrate of nickel in iodic acid, or by evaporating to dryness a solution of 1 pt. sulphate of nickel and 1½ pt. iodate of sodium, and dissolving out the sulphate of sodium from the residue with water. From a hot-saturated solution, it separates as a light-green crystalline powder. It dissolves in 77½ pts. of boiling and 120½ pts. of cold water. When ignited, it leaves pure oxide of nickel. Ammonia dissolves it readily, forming a blue liquid, from which alcohol throws down blue crystals, or a crystalline powder, consisting of *iodate of nickel-diammonium*, $NiIO^3.2NH^3 = IO^3.N\left\{\begin{matrix}NH^3Ni\\H^3\end{matrix}\right.$.

Iodates of Potassium.—1. *Mono-iodate or Normal Iodate.* This salt is prepared: 1. By adding iodine to solution of potash till a brown colour is produced, evaporating to dryness, and dissolving out the iodide of potassium formed at the same time with alcohol of specific gravity 0·81:

$$6KHO + I^6 = KIO^3 + 5KI + 3H^2O.$$

Should the iodate thus obtained contain carbonate of potassium, the latter must be decomposed by acetic acid, the whole evaporated, and the acetate of potassium removed by alcohol.

2. By dissolving trichloride of iodine in potash, the products being iodate, iodide and chloride of potassium:

$$12KHO + 3ICl^3 = 2KIO^3 + 9KCl + KI + 6H^2O.$$

The iodide and chloride are dissolved out by alcohol, as in the former process, but the latter, being less soluble, is more difficult to remove.

3. By melting iodide of potassium in a crucible, leaving it to cool till it becomes semifluid, and then gradually adding 1½ pts. chlorate of potassium. The mass becomes fluid, swells up, and solidifies to a spongy mass of iodate and chloride of potassium. It is dissolved in hot water, the iodate left to crystallise, the crystals redissolved in hot water and the iodate precipitated by alcohol.

Mono-iodate of potassium forms small white cubic crystals (Gay-Lussac); $\infty O\infty\ .\ \infty O$ (Marignac), but it is not easy to obtain distinct crystals. Specific gravity 3·979 (water at 17·5° = 1) (Kremers). It dissolves in 13 pts. water at 14° (Gay-Lussac); in 19·02 pts. water at 0·5°, in 14·85 pts. at 9·4°, in 10·77 pts. at 22·2°, in 5·95 pts. at 45·8°, and in 3·67 pts. at 69·2°. An aqueous solution of specific gravity 1·0741 at 19·5° contains 9·08 pts. KIO^3, for every 100 pts. water. The saturated aqueous solution boils at 102° (Kremers, Pogg. Ann. xciv. 271; xcv. 121; xcvii. 5). More soluble in aqueous iodide of potassium than in water. Insoluble in alcohol of specific gravity 0·81. Soluble in warm sulphuric acid without decomposition of the iodic acid. (Berzelius.)

At a low red heat, the salt melts and froths up, and is converted, with loss of

22·59 per cent. oxygen into iodide of potassium (**Gay-Lussac**). If only part of the oxygen is expelled, the residue consists of iodide and iodate, without any periodate (**Rammelsberg**). It deflagrates with a purple light on glowing charcoal.

The aqueous solution exhibits with sulphydric acid and other reducing agents, the reactions already described for iodates in general (p. 301). From a solution of the salt mixed with iodide of potassium, the stronger acids precipitate iodine. With strong hydrochloric acid, it yields water, free chlorine, and chloride of iodine and potassium:

$$KIO^3 + 6HCl = 3H^2O + Cl^2 + KICl^4.$$

A solution of iodate of potassium in excess of boiling nitric acid yields crystals of iodic acid on cooling, while nitre remains in solution; if however it is evaporated to dryness, one half the nitre formed is decomposed, and there remains a mixture of 1 atom of nitrate and 1 atom of di-iodate of potassium. When greater heat is applied, all the nitric acid is decomposed into pernitric oxide and oxygen, and driven off, so that the residue consists merely of iodate of potassium. (**Penny**, Ann. Ch. Pharm. xxxvii. 203.)

Double-salt of Iodate and Acid Sulphate of Potassium, $KIO^3.KHSO^4$.—This salt separates after the tri-iodate (p. 305) from a solution of the mono-iodate mixed with sulphuric acid. It was first obtained by **Serullas** (Ann. Ch. Phys. [2] xliii. 113), who regarded it as a compound of the di-iodate with anhydrous di-sulphate of potassium. **Millon** (Ann. Ch. Phys. [3] ix. 497) supposed it to be a compound of mono-iodate and monosulphate of potassium, $2KIO^3.K^2SO^4$. The formula above given was determined by **Marignac** (Ann. Min. [5] ix. 1), who obtained it of the same composition, even when the proportions between the sulphuric acid, iodic acid and potash in the solution were varied. The crystals are monoclinic, exhibiting the combination ∞P . ∞P2 . ∞P3 . ∞P∞ . oP . −P . −P2 . −P∞ . +P∞ (predominating at the ends) +3P∞ . (P∞) . (½P∞). Angle ∞P : ∞P in the clinodiagonal principal section = 54° 53′; ∞P2 : ∞P2 in the same = 92° 10′; oP : ∞P = 91° 29′; oP : ∞P∞ = 93° 14′; ∞P∞ : +P∞ = 115° 50′; ∞P∞ : −P∞ = 120° 42′ (**Marignac**). When heated to redness, they give off oxygen and iodine and leave sulphate and iodide of potassium.

Di-iodate, $2KIO^3.I^2O^5$ or $K^2O.2I^2O^5$.—Obtained—1. By mixing the aqueous solution of the mono-iodate with hydrochloric acid, and precipitating with alcohol.—2. By partially saturating an aqueous solution of trichloride of iodine with caustic potash or carbonate of potassium, whereupon the mixture becomes heated, and on cooling deposits a compound of the di-iodate with chloride of potassium (the mother-liquor saturated with potash still yields the mono-iodate). The solution of this compound, largely diluted with water, and evaporated in the air at 25°, yields the di-iodate in beautiful transparent right rhombic prisms, with dihedral summits, having a sour, astringent taste, and acid reaction.

According to **Marignac** (Jahresb. 1856, p. 297), the crystals contain $K^2O.2I^2O^5.H^2O$, and exhibit three essentially different forms, one trimetric, the other two monoclinic, the occurrence of which is independent of the temperature of crystallisation. The trimetric crystals, which separate only from solutions containing a small quantity of the mono-iodate, exhibit chiefly the combination ∞P . ∞P̆∞ . ∞P̄∞ . oP . ½P . ⅓P . ½P̄∞ . ¼P̆∞. Angle ∞P : ∞P = 82° 10′; P : P in the macrodiagonal principal section = 87° 10′; in the brachydiagonal = 101° 40′; oP : P = 106° 4′; oP : ⅓P̄∞ = 127° 23′; oP : ¼P̆∞ = 146° 48′. No cleavage. According to **Schabus** (Jahresber. 1854, p. 310), the combination is oP (predominant) . P . ⅔P . P̄∞ . ½P̆∞ . ∞P . ∞P̆∞ . ∞P̄∞. For P, the ratio of principal and secondary axes is 1 : 0·8973 : 0·7819. Angles P : P in the the terminal edges = 111° 13′ and 121° 2′; in the lateral edges = 97° 2′; ∞P : ∞P = 82° 4′. Cleavage imperfect parallel to oP.—The second form, which is monoclinic, separates, according to Marignac, chiefly from solutions containing a slight excess of acid. According to Schabus, the predominant combination is ∞P2 . ∞P∞ . oP . +P . −P. The principal axis, clino- and ortho-diagonals, are in the proportion 1 : 1·7307 : 0·8627. Angle of the inclined axes = 87° 16′. ∞P2 : ∞P2 in the clinodiagonal principal section = 78° 48′; oP : −P = 129° 22′; oP : +P = 128° 9′. The crystals are often joined as twins, the face of combination being apparently parallel to +½P∞. Marignac has also measured these crystals, viewing them in a different direction, so that the faces oP, ∞P∞, ∞P2, &c. in the preceding determination, become respectively ∞P∞, oP, (½P∞), &c. in that of Marignac. Regarded thus, the crystals exhibit the faces oP . ∞P∞ . ∞P2 . −P . (P∞) . (½P∞), with several subordinate clinodiagonal domes and hemipyramids. ∞P2 : ∞P2 in the clinodiagonal principal section = 120° 17′; −P : −P in the same = 87° 48′; oP : (P∞) = 110° 53′; oP : (½P∞) = 127° 20′; oP : ∞P∞ = 91° 56′. The crystals are almost always intersecting twins, with the face of combination −P∞; rarely contact-twins joined by the face oP. Cleavage parallel to oP.—The third form, which accompanies the other two, is also monoclinic, the crystals being mostly aggregated, and exhibiting the combination $oP \,.\, \infty P \,.\, +P\infty \,.\, -P\infty \,.\, -\frac{1}{2}P\infty \,.\, (P\infty) \,.\, (2P\infty) \,.\, -P$. Angle $\infty P : \infty P$ in the clinodiagonal principal section = 99° 30′; $oP : -P$ = 122°; $oP : \infty P$ = 96° 40′; $oP : -P\infty$ = 129° 28′; $oP : +P\infty$ = 117° 16′ (Marignac). Rammelsberg, who formerly regarded the crystals as anhydrous, found, by a later determination (Jahresb. 1857, p. 125), that they contain $2(K^2O.2I^2O^5).3H^2O$ [? in which form].

Di-iodate of potassium is soluble in 75 pts. water at 15°, insoluble in alcohol (Serullas). When heated, it gives off oxygen and vapour of iodine, and is converted, first into the mono-iodate, then into iodide. It deflagrates on glowing charcoal.

A double salt, consisting of *di-iodate and chloride of potassium*, $2KCl.2KIO^3.I^2O^5$, is obtained when an aqueous solution of trichloride of iodine is not quite saturated with potash, and the solution is left to evaporate:

$$4KHO + 8ICl^3 + 7H^2O = (2KCl.2KIO^3.I^2O^5) + 4ICl + 18HCl;$$

or by heating mono-iodate of potassium with dilute hydrochloric acid:

$$4KIO^3 + 2HCl = (2KCl.2KIO^3.I^2O^5) + H^2O.$$

It forms shining transparent prisms and elongated four-sided tables with truncated terminal edges (Serullas, Ann. Ch. Phys. [2] xliii. 121). According to Millon (*ibid.* [3] ix. 407) and Marignac (Jahresb. 1856, p. 298) the crystals contain 1 at. water. According to Rammelsberg (Pogg. Ann. xcvii. 92), who also finds them to be anhydrous, they are trimetric, exhibiting the combination $\infty P \,.\, \infty\bar{P}\infty \,.\, \infty\breve{P}\infty \,.\, \bar{P}\infty \,.\, \frac{1}{2}\bar{P}\infty \,.\, oP \,.\, \breve{P}2$. Angle $\infty P : \infty P$ in the macrodiagonal principal section = 82° 8′: $\bar{P}\infty : \bar{P}\infty$, in the same = 97° 0′; $\frac{1}{2}\bar{P}\infty : \frac{1}{2}\bar{P}\infty$, in the same = 132° 16′. Proportion of brachydiagonal, macrodiagonal, and principal axis = 0·8713 : 1 : 0·7709. The crystals are efflorescent, soluble in 19 pts. water at 15° (Serullas). Cold alcohol dissolves out the chloride of potassium, leaving the di-iodate. (Filhol, J. Pharm. xxv. 506.)

Di-iodate with *Di-sulphate of Potassium*, $K^2S^2O^7.K^2I^2O^{11}$?—This, according to Serullas, is the composition of the double salt obtained, after the separation of the tri-iodate, when a solution of the mono-iodate is mixed with sulphuric acid. But, according to Millon and Marignac, this salt contains, not the di-iodate, but the mono-iodate of potassium (p. 303).

Tri-iodate, $2KIO^3.2I^2O^5$ or $K^2O.3I^2O^5$.—This salt is obtained by mixing aqueous iodic acid with a small quantity of potash, or by adding a solution of the mono- or di-iodate to aqueous sulphuric, phosphoric, hydrochloric, nitric, or silicic acid. When a solution of the mono-iodate is heated with a large excess of dilute sulphuric acid, and left to evaporate at 25°, the tri-iodate crystallises out, leaving in solution a compound of iodate and acid sulphate of potassium.

The tri-iodate forms large transparent crystals—triclinic, according to Rammelsberg and Marignac—which, even when free from sulphuric acid, assume a reddish colour after a while. According to Serullas and Rammelsberg, they are anhydrous; according to Millon and Marignac, they contain 2 at. water: $K^2O.3I^2O^5.2H^2O$. The salt when melted gives off ⅔ of its iodine, leaving iodide of potassium. It dissolves in 25 pts. water at 15°. (Serullas, Ann. Ch. Phys. [2] xliii. 117.)

Basic Iodate?—According to Gay-Lussac, a solution of the mono-iodate mixed with potash deposits a salt containing excess of potash; but, according to Rammelsberg, nothing but the mono-iodate crystallises out.

Iodate of Silver, $AgIO^3$, obtained by precipitating nitrate of silver with iodic acid or iodate of sodium, is white, insoluble in water, nearly insoluble in dilute nitric acid, easily soluble in ammonia, the solution yielding by spontaneous evaporation, pure iodate of silver in monoclinic crystals, which, according to Marignac (Ann. Min. [5] ix. 1), exhibit the faces $\infty P \,.\, \infty P\infty$, inclined to one another at an angle of 127½°, and a number of other faces at the ends of the prism, extending in a direction parallel to the orthodiagonal. Sulphurous acid passed into the solution of the salt in ammonia, is converted into sulphuric acid, and throws down iodide of silver. Hydrochloric acid decomposes it readily, yielding chloride of silver, chloride of iodine, and free chlorine.

Iodates of Sodium.—The *mono-iodate*, $NaIO^3$ or $Na^2O.I^2O^5$, is obtained: 1. By passing chlorine gas to saturation through 10 pts. of water containing 1 pt. of iodine diffused through it; neutralising the liquid with carbonate of sodium; passing chlorine again through it, in order to dissolve the iodine thus thrown down; again neutralising with the carbonate; redissolving the iodine thus separated by means of chlorine, and so on. The liquid is then evaporated to $\frac{1}{10}$th its bulk, mixed, while still warm, with half its volume of alcohol, and the compact crystalline mass, consisting of eight-sided prisms, produced on cooling, is freed from adhering chloride of sodium by washing with alcohol (Liebig, Pogg. Ann. xxiv. 362). An excess of carbonate of sodium must be avoided; otherwise, basic periodate of sodium will be formed (Magnus and Ammermüller). According to Duflos (Schw. J. lxii. 390), the addition of alcohol is unnecessary, as the less soluble iodate can be separated from the chloride of sodium by crystallisation.—2. By partially saturating aqueous trichloride of iodine with caustic soda or carbonate of sodium, precipitating with alcohol, washing the precipitate with the same liquid, and recrystallising from hot water. (Serullas.)

Mono-iodate of sodium separates from an aqueous solution left to evaporate in moderately warm air (Rammelsberg), or from a hot concentrated solution on cooling (Penny), in crystals containing 1 at. water: $NaIO^3.H^2O$. This hydrate forms tufts of fine silky needles, which, if the temperature falls below 5°, while they are still immersed in the liquid, are converted into the pentahydrated crystals. They give off all their water at 180° (Rammelsberg, Penny). The pentahydrated salt, $NaIO^3.5H^2O$, obtained by spontaneous evaporation below 5°, forms octagonal prisms of the trimetric system, with pyramidal summits, the combination being $\infty P . \infty \bar{P}\infty . \infty P\infty . P$, with $\breve{P}\infty$ subordinate. Axes $a : b : c = 0·9534 : 1 : 0·6607$ (ii. 144). Angles $P : P$ in the terminal edges = 119° 56′ and 123° 30′; in the lateral edges = 87° 30′; $\infty P : \infty P$ = 92° 45′ and 87° 15′. The crystals are prismatically elongated in the direction of the principal axis, the faces ∞P being almost always unequally developed. When exposed to the air, they give off 4 at. water and are converted into the monohydrated salt (Rammelsberg, Pogg. Ann. xliv. 548; xc. 12). According to Millon (Ann. Ch. Phys. [3] ix. 400), crystals containing 2, 3, 6, and 8 at. water are also obtained, under special circumstances. Penny (Ann. Ch. Pharm. xxxvii. 203), by cooling a somewhat dilute solution, obtained crystals containing $NaIO^3.3H^2O$.

The anhydrous salt, obtained by drying the crystals at 150°, dissolves in 13·8 pts. of water at 14·5°, but is insoluble in alcohol (Gay-Lussac). According to Kremers (Pogg. Ann. xcvii. 5, 8), it dissolves in 39·75 pts. water at 0°, in 11·03 pts. at 20°, in 6·95 pts. at 40°, in 4·79 pts. at 60°, in 3·61 pts. at 80°, and in 2·95 pts. at 100°. The saturated solution boils at 102°. A solution of specific gravity 1·0698 at 19·5° contains 8·13 pts. of the anhydrous salt for every 100 pts. of water. (Kremers, Pogg. Ann. xcix. 444.)

Mono-iodate of sodium melts when heated, and while still below redness, gives off 24·45 per cent. oxygen, together with iodine, leaving a mixture of iodide of sodium and soda (Gay-Lussac). According to Liebig, it leaves a hypo-iodite of sodium containing $2Na^2O.I^2O$ or $Na^4I^2O^3$; when heated to redness, it yields 24·21 per cent. of oxygen, and 75·79 of iodide of sodium (Benckiser). It detonates on glowing charcoal, and slightly when mixed with sulphur and struck (Gay-Lussac). It is decomposed by concentrated hydrochloric acid into water, chlorine, and a yellow liquid, which probably contains trichloride of iodine and sodium, $NaCl.ICl^3$, but does not yield this compound in a crystalline form (Filhol, J. Pharm. xxv. 440). Heated with a little nitric acid, it yields di-iodate, and with a larger proportion, tri-iodate of sodium in the anhydrous state (Penny). When dissolved hot in a mixture of equal quantities of sulphuric acid and water, it gives, by evaporation, crystals which, when placed on bibulous paper and nearly dry, become all at once fluid and tenacious. (Liebig.)

Double Salts of Mono-iodate of Sodium.—1. With *bromide of sodium*, $2NaBr.NaIO^3.9H^2O$.—Obtained by dissolving the iodate in a hot strong solution of bromide of sodium. It crystallises, by cooling or spontaneous evaporation, in aggregations of extremely fine, colourless, transparent, six-sided laminæ, apparently rhombohedral combinations. It is easily soluble in water. When heated, it gives off a large quantity of water, melts, gives off oxygen mixed with iodine, and leaves a mixture of bromide and iodide of sodium. Two-thirds of the water is given off over sulphuric acid. (Rammelsberg, J. pr. Chem. lxxxv. 436; Rép. Chim. pure, 1862, p. 251.)

2. *With Chloride of Sodium*, $3NaCl.2NaIO^3.9H^2O$.—(1.) When chlorine is passed through a solution of iodate of sodium mixed with a rather large quantity of caustic soda as long as basic periodate of sodium (p. 310) continues to separate, the decanted liquid, when left at rest, deposits crystals of chloride of sodium, first combined with iodate of sodium, then by itself, and afterwards mixed with chlorate of sodium.—(2.) The mother-liquor obtained in the second mode of preparing mono-iodate of sodium (see above) deposits, at a higher temperature and greater degree of concentration, crystals of the compound of iodate and chloride. The crystals, which are large, colourless, and often transparent, belong to the triclinic system, and are sometimes triclinic pyramids having all their edges and summits truncated, frequently, also, modified by various pyramidal faces. They also form twins joined by the basal end-faces, and giving the crystal a tabular character. The axes *a*, *b*, *c* of the pyramid (*c* being the principal axis) are to one another as 1·1309 : 1 : 1·10436. The inclinations of the principal sections are by direct measurement, $\infty \breve{P}\infty : \infty \bar{P}\infty$ = 97° 16′; $oP : \infty \bar{P}\infty$ = 104° 0′; $oP : \infty \breve{P}\infty$ = 100° 63′. Inclinations of the axes, by calculation, $b : c$ = 102° 57′; $a : c$ = 99° 9′; $a : b$ = 94° 56′. The crystals are not efflorescent, but when heated, they give off their water, and melt to a clear liquid which gives off nothing but oxygen gas, and when very strongly heated, leaves a mixture of iodide and chloride of sodium. Water extracts the chloride of sodium, leaving the iodate with 1 at. water. (Rammelsberg, Pogg. Ann. xliv. 548; cxv. 584.)

3. *With Iodide of Sodium*, $NaI.NaIO^3.10H^2O$ (Mitscherlich); $3NaI.2NaIO^3.19H^2O$ (Penny); $3NaI.2NaIO^3.20H^2O$ (Marignac).—This compound, discovered by Mitscherlich (Pogg. Ann. xi. 162; xvii. 481), is obtained by dissolving iodine in a cold and not very concentrated aqueous solution of caustic soda (or the carbonate, according to Penny) till it begins to turn brown, then leaving it in a cold place till it crystallises. Prisms of pure iodate of sodium then first appear, but afterwards redissolve, and are replaced by this compound (Mitscherlich). The same crystals are produced in a few days by immersing crystals of iodate of sodium in a strong solution of the iodide, and leaving the liquid to itself at a temperature not above 15° (Penny, Ann. Ch. Pharm. xxxvii. 202). The crystals are hexagonal tables, $oR . \infty R$, with $+R$, $-\frac{1}{2}R$ and other faces. Angle $oR : R = 115° 7'$; $oR : -\frac{1}{2}R = 133° 10$ (Marignac, Jahresb. 1857, p. 124). When heated they first give off water, then oxygen, with a trace of iodine. Cold water dissolves them without decomposition, but alcohol dissolves the iodide of sodium, leaving the iodate.

Acid Iodates of Sodium.—When an aqueous solution of trichloride of iodine is mixed, first with mono-iodate of sodium, then with alcohol, the di-iodate separates out, but this salt, if dissolved in water and evaporated, yields crystals of the mono-iodate, and an acid mother-liquor (Serullas, Ann. Ch. Phys. xlv. 59). By evaporating also a mixture of the iodate with excess of iodic acid, the neutral salt crystallises out first, and then the iodic acid (Rammelsberg). Penny obtained a di-acid and tri-acid salt, by treating the mono-iodate with nitric acid.

Iodate of Tin.—Iodate of sodium forms, with dichloride of tin, a precipitate which is white at first, but soon turns yellow, brown and grey, yielding tetrachloride and dioxide of tin and free iodine.

Iodates of Uranium.—The *uranic salt*, $U^4O^3.I^2O^5.5H^2O$ or $2(U^2O)IO^3.5H^2O$, is obtained, by double decomposition, as a yellow precipitate which dissolves with difficulty in nitric acid, leaves uranoso-uranic oxide when ignited, and is decomposed by potash. *Uranous iodate* is obtained by precipitation from uranous chloride, as a greyish-green substance, which soon decomposes, being partially converted into the uranic salt.

Iodate of Yttrium.—Precipitable from concentrated solutions; remains as a crystalline crust on evaporation. It is anhydrous, dissolves in 160 pts. water, and when suddenly heated, decomposes with explosion and deflagration.

Iodate of Zinc, $ZnIO^3.H^2O$.—To prepare this salt, a solution of sulphate of zinc and iodate of sodium in equivalent proportions is evaporated to dryness, and the resulting sulphate of sodium is dissolved out by water. Iodate of zinc then remains as a white powder, soluble in 75·9 pts. of hot, and 113·8 pts. of cold water, soluble also in nitric acid and in ammonia. The ammoniacal solution yields by spontaneous evaporation, or on addition of alcohol, a crystalline salt consisting of $3ZnIO^3.4NH^3$ or $3(NH^3Zn)IO^3.NH^3$. It is decomposed by water, with separation of oxide of zinc.

Iodate of zinc leaves oxide of zinc when ignited.

Periodic Acid, Anhydride and Salts.

Periodic or Hyperiodic acid. HIO^4 or $H^2O.I^2O^7$, or according to Langlois, H^5IO^6 or $5H^2O.I^2O^7$. (Magnus and Ammermüller, Pogg. Ann. xxviii. 514.—Benckiser, Ann. Ch. Pharm. xvii. 254.—Langlois, Ann. Ch. Phys. [3] xxxiv. 257; Jahresb. 1852, p. 345.)—This acid, which was discovered by Magnus and Ammermüller (Pogg. Ann. xxviii. 514), is produced, in the form of a disodic salt, by the action of chlorine on a solution of iodate of sodium mixed with carbonate of sodium or caustic soda:

$$\underset{\substack{\text{Sodic}\\ \text{iodate.}}}{NaIO^3} + 3NaHO + Cl^2 = \underset{\substack{\text{Disodic}\\ \text{periodate.}}}{Na^2H^3IO^6} + 2NaCl.$$

A good method of preparing it is to add 1 pt. of iodine to a solution of 7 pts. carbonate of sodium in 100 pts. water, and pass chlorine into the heated liquid as long as a precipitate continues to form. This precipitate, which consists of disodic periodate, is dissolved in nitric acid perfectly free from nitrous acid; nitrate of silver is then added; the resulting yellow precipitate of diargentic periodate is dissolved in hot dilute nitric acid; and the solution is concentrated at a moderate heat, till the monargentic periodate, $AgIO^4$, crystallises out; this salt, separated from the mother-liquor, is treated with cold water, which extracts half the periodic acid, reproducing the diargentic periodate; and the filtered solution is evaporated: pure periodic acid then crystallises out (Magnus and Ammermüller). Another method is to precipitate the solution of the disodic salt in nitric acid with nitrate of lead, decompose the precipitate of periodate of lead with somewhat less than an equivalent quantity of dilute sulphuric acid, and concentrate the filtrate by evaporation (Benckiser). According to Langlois, however, the acid thus obtained is always contaminated with iodic acid.

The acid may likewise be obtained by igniting iodate of barium, which then gives off iodine and oxygen, and is converted into pentabasic periodate of barium—and decomposing that salt with sulphuric acid. But this method is not advantageous, because a considerable portion of the iodic acid is completely resolved by the heat into iodine and oxygen.

The iodates of the alkali-metals give off the whole of their oxygen when heated, and are converted into iodides; consequently periodic acid cannot be prepared in the same manner as perchloric acid (i. 910).

Periodic acid separates from its aqueous solution by evaporation, at a gentle heat, in colourless crystals, apparently having the form of oblique rhombic prisms, which deliquesce quickly in moist air, melt at 130°, and at 160° give off their water, leaving a white mass of periodic anhydride, I^2O^7, which, at 180° or 190°, gives off oxygen with great rapidity, leaving iodic anhydride (Benckiser). The crystals are rhombic prisms, having the composition $H^5IO^6 = HIO^4.2H^2O$ or $5H^2O.I^2O^7$. They melt at 130°, and between 200° and 210°, give off 5 at. water and 2 at. oxygen, and are reduced to iodic anhydride, I^2O^5, which at a higher temperature is completely resolved into iodine and oxygen. (Langlois.)

Periodic acid dissolves very easily in *water*, sparingly in *alcohol* and in *ether*, in which solutions it is slowly reduced to iodic acid. It is likewise reduced by many other *organic substances*, and instantly by *hydrochloric*, *sulphurous*, or *sulphydric acid*. With hydrochloric acid it forms water, chloride of iodine, and free chlorine. *Sulphur* is not oxidised by it; but *phosphorus* is partly converted into phosphoric acid—for the most part, however, into oxide of phosphorus. *Metals* are oxidised by the solution, forming basic periodates. It forms a precipitate with *tannic acid*, a reaction which distinguishes it from iodic acid. The precipitate dissolves in potash and in ammonia, with dark red colour, arising from the oxidation of the tannic acid, the iodine at the same time uniting with the alkali-metal. (Langlois.)

Periodates.—Periodic acid is generally regarded as monobasic, like perchloric acid, the formula of its normal salts being MIO^4 or $M^2O.I^2O^7$. Only four of these anhydrous monometallic periodates are however known, namely those of ammonium, potassium, sodium, and silver. All other periodates contain a larger proportion of base, and may be derived from the crystallised acid H^5IO^6, regarded as $HIO^4.2H^2O$, by the replacement of the water of crystallisation by a metallic oxide or hydrate, thus:

HIO^4 .	H^2O .	H^2O . .	Periodic acid.
$(NH^4)IO^4$.	H^2O .	H^2O . .	Mono-ammonic periodate.
$NaIO^4$.	$NaHO$.	H^2O . .	Disodic periodate.
$PbIO^4$.	Pb^2O .	H^2O . .	Triplumbic periodate.
$CuIO^4$.	Cu^2O .	$CuHO$ . .	Tetracupric periodate.
$BaIO^4$.	Ba^2O .	Ba^2O . .	Pentabarytic periodate.

The existence of the monohydric acid HIO^4 must however for the present be regarded as hypothetical, the only hydrate whose constitution has been established by analysis being the pentahydric acid, H^5IO^6, analysed by Langlois; and from this, regarded as a pentatomic molecule, $\left.\begin{matrix}(IO)^v\\H^5\end{matrix}\right\}O^5$, the greater number of the periodates may be derived by the partial or total replacement of the hydrogen by metals. The anhydrous periodates of potassium, silver, and sodium, (MIO^4) may then be regarded as metaperiodates, bearing to the orthoperiodates, M^5IO^6, a relation similar to that of metaphosphoric to orthophosphoric acid. There are a few periodates which cannot be included in either of the preceding formulæ, viz. a barium-salt containing $5Ba^2O.2I^2O^7$ or $3Ba^2O.4BaIO^4$, a potassium-salt containing $2K^2O.I^2O^7$ or $K^2O.2KIO^4$, and a silver-salt containing $2Ag^2O.H^2O.I^2O^7$ or $Ag^2O.HIO^4$.

The monometallic periodates are resolved by heat into oxygen and metallic iodide; the polymetallic salts into a mixture of iodide and oxide or reduced metal. Most periodates are sparingly soluble or insoluble in water, but they all dissolve easily in dilute nitric acid. The solution of the monosodic salt, added to a solution of a barium-, calcium-, lead-, or silver-salt, precipitates the polymetallic or basic periodates of these bases, the liquid acquiring an acid reaction.

Periodate of Ammonium, $(NH^4)IO^4.2H^2O$, separates on mixing the solutions of ammonia and periodic acid. It dissolves in a large quantity of water, and the solution, evaporated at a gentle heat, yields crystals, apparently having the form of rhombic prisms. It has an acid reaction, and explodes when heated in a tube. (Langlois.)

Periodates of Barium.—The monobarytic salt is not known. A *pentabarytic* or *pentabasic* salt, Ba^5IO^6 or $5Ba^2O.I^2O^7$, is obtained by igniting iodate of barium or a mixture of iodide and peroxide of barium, and dissolving out the iodide of barium from the residue with water. Its solution in nitric acid yields with nitrate of silver a yellow-brown precipitate of basic periodate of silver. (Rammelsberg, Pogg. Ann. xliv. 272.)

A salt containing half as much base as the last, viz. $2Ba^5IO^6.I^2O^7$ or $5Ba^2O.2I^2O^7$, is precipitated by ammonia from the solution of the pentabasic salt, or from a mixture of a soluble barium-salt with monobasic periodate of sodium dissolved in nitric acid; also on mixing nitrate of barium with dibasic periodate of sodium. The precipitate contains 5 at. water, which are given off at 100°; by longer exposure to this temperature, the salt is completely converted into iodate of barium. (Rammelsberg.)

A *dibarytic* or *dibasic* salt, $Ba^2H^3IO^6$ or $2Ba^2O.3H^2O.I^2O^7$, is obtained by adding baryta-water to a solution of the corresponding sodium-salt mixed with a few drops of nitric acid. It is a white precipitate which decomposes at a red heat, yielding the pentabarytic salt (Langlois):

$$10Ba^2H^3IO^6 = 4Ba^5IO^6 + I^6 + O^{21} + 15H^2O.$$

Periodates of Calcium.—A *dicalcic salt*, $Ca^2H^3IO^6$ or $2Ca^2O.3H^2O.I^2O^7$ (at 100°), is obtained by decomposing the sodium-salt, NaH^4IO^6, with nitrate of calcium, as a white precipitate, which appears crystalline under the microscope, and when heated, gives off water, oxygen, and iodine, and leaves the pentacalcic salt, Ca^5IO^6 (Langlois). The latter is likewise obtained, but mixed with lime, by igniting iodate of calcium in a close vessel.

Periodate of Copper, Cu^4HIO^6 or $4Cu^2O.H^2O.I^2O^7$, is precipitated by mixing the solutions of sulphate of copper and the monosodic salt—a considerable quantity, however, remaining in solution—or by the action of aqueous periodic acid in slight excess on hydrated carbonate of copper. (Langlois.)

Periodates of Iron.—Iron-salts (ferrous or ferric) form, with solution of periodate of sodium, yellowish white precipitates, easily soluble in nitric acid (Benckiser). According to Langlois, periodic acid, in contact with ferrous oxide, is reduced to iodic acid, and ferric iodate separates out. Similar reaction with manganous oxide.

Periodates of Lead.—A *triplumbic* or *tribasic salt*, $Pb^3H^2IO^6$ or $3Pb^2O.H^2O.I^2O^7$, is precipitated on mixing 1 at. of the disodic salt with 3 at. nitrate of lead, in microscopic crystals, which do not suffer any loss of weight between 120° and 130°, but, at a higher temperature, give off water, oxygen, and iodine, and leave an oxyiodide of lead containing $2PbI.5Pb^2O$ (Langlois):

$$4Pb^3H^2IO^6 = 2PbI.5Pb^2O + O^{15} + I^2 + 4H^2O.$$

Periodate of Lithium, Li^5IO^6?—By treating carbonate of lithium with periodic acid and evaporating the solution at a gentle heat, a crystalline mass is obtained, which dissolves completely in water, and when dried in a vacuum, and then heated to redness, gives off successively water, oxygen, and iodine, but without undergoing complete decomposition. (Langlois.)

Periodate of Magnesium.—Magnesium-salts are not precipitated by solution of periodate of sodium. Carbonate of magnesium, immersed in aqueous periodic acid, is converted into insoluble periodate of magnesium, which dissolves, however, in excess of the acid. The salt consists of small prismatic crystals, which, when dried at mean temperatures, contain $2Mg^2H^3IO^6.9H^2O$ or $2Mg^2O.3H^2O.I^2O^7 + 9$ aq., give off 9 at. water, at 100°, and leave pure magnesia when ignited. (Langlois.)

Periodates of Potassium.—The *monopotassic salt*, KIO^4, is precipitated in sparingly soluble crystalline grains on passing chlorine into a solution of the iodate mixed with potash or carbonate of potassium. Its aqueous solution, mixed with caustic potash, yields the *tetrapotassic salt*, $K^2O.2KIO^4$ or $2K^2O.I^2O^7$, which is also sparingly soluble in water, and is converted by ignition into a mixture of potash and iodide of potassium. The neutral salt when ignited leaves the pure iodide. (Magnus and Ammermüller.)

Periodates of Silver.—Nitrate of silver added to a solution of disodic periodate, throws down a greenish yellow precipitate which is a basic periodate of silver. By washing it with water containing nitric acid, then dissolving it nearly to saturation in warm nitric acid, and evaporating by heat, the *monoargentic salt*, $AgIO^4$, is obtained in anhydrous orange-yellow crystals. This salt is decomposed by warm water, which dissolves out half the acid, leaving a blackish brown residue of the *tetrargentic salt*, $2Ag^2O.I^2O^7.H^2O$ or $Ag^2O.2AgIO^4.H^2O$, which turns red by trituration. Cold water decomposes the salt in like manner, but the residual salt is a yellow powder, consisting of $Ag^2H^3IO^6$ or $2Ag^2O.3H^2O.I^2O^7$, and separates from a solution in dilute slightly warmed nitric acid, in straw-yellow crystals, which, according to Rammelsberg

(Jahresb. 1857, p. 125), are rhombohedral, exhibiting the combination $R \,.\, -\tfrac{1}{2}R \,.\, oR$. For R, the ratio of the secondary axes to the principal axis = 1 : 2·0653. Angle R : R in the terminal edges = 74° 0′; oR : R = 112° 45′. The crystals become darker-coloured by exposure to light. On pouring boiling water on these crystals or on the yellow powder, 2 atoms of water are removed, and the red salt above mentioned is produced. (Magnus and Ammermüller.)

Periodates of Sodium.—The *monosodic* salt, $NaIO^4$, is obtained by saturating the disodic salt with periodic acid, and evaporating. It is colourless, very soluble in water, anhydrous, crystallises readily, and is permanent in the air (Magnus and Ammermüller). The crystals are dimetric, $P \,.\, P\infty$. For P, the ratio of the secondary axes to the principal axis is 1 : 1·59. Angle P : P in the terminal edges = 99° 30′; in the lateral edges = 132° 4′. The crystals are colourless. (Rammelsberg, *loc. cit.*)

The *disodic* or *dibasic* salt, $Na^2H^3IO^6$ or $2Na^2O.3H^2O.I^2O^7$, is obtained by passing chlorine gas into a hot solution of 1 pt. iodine and 7 pts. carbonate of sodium in 100 pts. water, or into a solution of 1 pt. iodate of sodium mixed with 3 pts. of caustic soda (Magnus and Ammermüller). Langlois uses equal weights of caustic soda and the iodate, and to obtain a solution as concentrated as possible, first dissolves the caustic soda in water, then adds the iodate, and surrounds the filtered solution with hot water while the chlorine is passing into it; the sodic periodate then separates in considerable quantity, as a crystalline powder, having the composition just mentioned. It is sparingly soluble in cold water, somewhat more in warm water, and may be obtained in the crystalline form from a boiling solution of the neutral salt mixed with caustic soda. At a white heat, it gives off 3 at. water and 8 at. oxygen, and leaves an oxyiodide of sodium:

$$2Na^2H^3IO^6 - 3H^2O - O^8 = Na^4I^2O.$$

At a low red heat, it loses only 3 at. oxygen, leaving a residue of *hypo-iodite* of sodium, $Na^4I^2O^3 = 2Na^2O.I^2O$ (or perhaps a compound of iodide and *iodite* of sodium, $2NaI + 3Na^2O.I^2O^3$ or $NaI.Na^2O.NaIO^2$). This compound is sparingly soluble in water, has an alkaline reaction, and bleaches vegetable colours, but loses this property when boiled with water, iodate of sodium being then formed, and the salt becoming easily soluble. On exposure to the air it turns moist, and gradually yields free iodine.

Periodate of Zinc.—Hydrated carbonate of zinc is converted by aqueous periodic acid into a granular powder of periodate of zinc, Zn^4HIO^6 or $4Zn^2O.H^2O.I^2O^7$, which dissolves readily in excess of the acid, forming a solution, which, when evaporated at a gentle heat, yields laminar crystals of another salt containing $3Zn^2O.7H^2O.2I^2O^7$, *i.e.* a double per-iodic molecule, $Zn^3H^7I^2O^{12} = \left.\begin{matrix}(\overset{''''}{I}O)^2 \\ Zn^3H^7\end{matrix}\right\}O^{10}$. (Langlois.)

IODINE, SELENIDE, SULPHIDE, and **TELLURIDE OF.** See Selenium, Sulphur, and Tellurium, Iodides of.

IODITE, IODOPYRITE, IODIC SILVER. Native iodide of silver. (See Silver, Iodide of.)

IODOBENZOIC ACID. $C^7H^5IO^2$.—An acid produced by the action of hydriodic acid on diazobenzo-oxybenzamic acid:

$$\underset{\substack{\text{Diazobenzo-}\\\text{oxybenzamic}\\\text{acid.}}}{C^{14}H^{11}N^3O^4} + 2HI = \underset{\substack{\text{Hydriodate of}\\\text{oxybenzamic}\\\text{acid.}}}{C^7H^7NO^3.HI} + \underset{\substack{\text{Iodobenzoic}\\\text{acid.}}}{C^7H^5IO^2} + N^2.$$

It crystallises in needles, is heavier than water, easily soluble in alcohol; sublimes without decomposition; forms a white silver-salt, $C^7H^4AgIO^2$, insoluble in water and in alcohol; is converted by fuming nitric acid into nitro-iodobenzoic acid. (Griess, Ann. Ch. Pharm. cxiii. 201.)

IODOBRUCINE. Syn. with Iodide of Brucine. (See Brucine, i. 683.)

IODO-CAOUTCHIN. See Caoutchin (i. 737).

IODO-CHLORO-NITROHARMINE. Syn. with Di-iodide of Chloro-nitro-harmine. (See Harmine, iii. 12).

IODOCINCHONINE. See Cinchonine (i. 979).

IODOCINNAMIC ACID. $C^9H^7IO^2$?—When cinnamic acid is melted with excess of iodine, and the dark brown mass is boiled with water till all the free iodine is volatilised, the liquid on cooling yields small colourless stellate crystals of iodocinnamic acid, which acquire a faint yellow colour on exposure to the air. The acid dissolves easily in hot water and in alcohol. (Herzog, N. Br. Arch. xx. 147.)

IODOCODEÏNE. Syn. with Iodide of Codeïne. (See CODEÏNE, i. 1068).

IODOFORM. CHI^3. *Di-iodated iodide of methyl.* (Gm. vii. 330; Gerh. i. 609.) —This compound, which was discovered in 1824 by Serullas (Ann. Ch. Phys. xxv. 314), is produced by the action of iodine and alkalis or alkaline carbonates on wood-spirit, alcohol, or ether; in small quantity also by the action of the same substances on cane-sugar, glucose, gum, dextrin, and several albuminous substances. It has also been observed among the products obtained by heating glycerin with hydriodic acid. (Erlenmeyer, Jahresb. 1861, p. 668.)

Preparation.—1 pt. of alcohol is added to a solution of 2 pts. crystallised carbonate of sodium in 10 pts. water; the liquid is heated to 60 or 80°; and 1 pt. of iodine is added by small portions, till it is entirely dissolved, and the liquid has become colourless. Iodoform then makes its appearance towards the end of the operation and sinks to the bottom of the hot liquid, which must be filtered to collect this first portion of the product. The mother-liquor is then again heated to 60° or 80°; another portion of carbonate of sodium, equal to the former, is dissolved in it; a fresh portion of alcohol is added; and a current of chlorine is passed into the liquid, which must be continually agitated, so that the iodine which separates may mix well with it. When the process is so conducted that a slight excess of iodine is constantly present, iodoform is produced in abundance. When a considerable quantity has been deposited, the stream of chlorine is interrupted, the liquid is left to decolorise, and the second portion of iodoform is added to the first. The mother-liquor may then be treated with chlorine and a third portion of iodoform obtained. The process, when properly conducted, yields a quantity of iodoform weighing 40 or 50 per cent. of the iodine used. Care must be taken, throughout the operation, to avoid a great excess of iodine, as in that case the iodoform will not be produced at all. Borax may be used instead of carbonate of sodium, and will yield a product of equal amount. With phosphate of sodium the product is not so good. (Filhol, J. Pharm. [3] vii. 267.)

Cornelius and Gille (*ibid.* xxii. 196) prepare iodoform by adding hypochlorite of calcium to an alcoholic solution of iodide of potassium heated to 40°, continuing the addition till the liquid becomes colourless. It then on cooling yields a crystalline deposit, consisting of iodoform mixed with iodate of calcium, from which the iodoform may be dissolved by boiling alcohol. 8 pts. of iodide of potassium yield, by this process, 2 pts. of iodoform and 2 pts. of iodate of calcium.

Properties.—Iodoform crystallises in nacreous scales, friable, soft to the touch, having a sulphur-yellow colour and the odour of saffron. According to Rammelsberg and Kokscharow (Jahresber. 1857, p. 431), the crystals are hexagonal combinations oP . P. For P the ratio of the secondary axes to the principal axis is 0·9025 : 1. Angle P : P in the terminal edges = 133° 36′; in the lateral edges = 104°. Specific gravity about 2·0. Melts between 115° and 120°, and then vaporises, partly without alteration, partly resolved into iodine and hydriodic acid, with a residue of charcoal. With vapour of water it distils undecomposed. It is not perceptibly soluble in *water*, *acids*, or aqueous *alkalis*, but dissolves readily in *alcohol*, *ether*, and *oils*, both fixed and volatile.

Decompositions.—1. Iodoform heated in a sealed tube to 150°, either alone or with *iodine*, is resolved into di-iodide of methylene, and a number of brown substances not yet examined (Hofmann, Chem. Soc. J. xiii. 65).—2. Iodoform is acted upon by *bromine*, yielding bromiodoform, $CHBr^2I$.—3. With moist *chlorine*, it yields chlorocarbonic oxide, hydrochloric acid, and protochloride of iodine:

$$CHI^3 + H^2O + Cl^6 = COCl^2 + 3HCl + 3ICl.$$

—4. Heated with *pentachloride of phosphorus*, it yields an oily liquid, perhaps chloroform, or according to Butlerow, di-iodide of methylene, CH^2I^2.—5. Distilled with *chloride of mercury*, *lead*, or *tin*, it yields chloriodoform, $CHCl^2I$.—6. Distilled with *sulphide of mercury*, it yields a small quantity of an oily liquid, which, according to Bouchardat (J. Pharm. xxiii. 12) is sulphoform, C^2HS^3; but according to Eggert (Chem. Centr. 1857, p. 513) is nothing but disulphide of carbon.—7. With *cyanide of mercury* or *cyanide of silver* it yields a sublimate of iodide of cyanogen.—8. When *cyanogen gas* is passed into an alcoholic solution of iodoform, the liquid becomes heated and assumes a violet tint; and if then left at rest, deposits golden-yellow, prismatic crystals, from which alcohol extracts two substances having a strong metallic lustre; one with a greenish gold, the other with a violet colour; the latter appears to be *cyanide of di-iodomethyl*, $CHI^2.Cy$ (St.-Evre, Compt. rend. xxvii. 533).—9. Heated with alcoholic solution of *sulphocyanate of potassium* to 100° in sealed tubes, it yields a gas and oily compound which has an odour of horse-radish, and forms a crystalline compound with ammonia, though not so readily as oil of mustard (Hlasiwetz, Ann. Ch. Pharm. cxii. 184).—10. *Mercuric oxide* gently heated with iodoform acts energetically upon it, producing water, carbonic anhydride, formic acid, and mercuric iodide.—11. Iodoform boiled with *aqueous potash* is partly converted into formate and iodide of potassium, a portion, however, volatilising with the watery vapour.—12. With *alcoholic potash* it forms a liquid which Brüning, who first obtained it (Ann. Ch. Pharm. civ. 187) regarded as C^2HI^2O, but which, according to Butlerow, is di-iodide of methylene.—13. With *ethylate of sodium*, iodoform yields iodide of methylene, CH^2I^2, together with iodide of sodium and aldehyde (Butlerow, Ann. Ch. Pharm. cvii. 110):

$$C^2H^5NaO + CHI^3 = CH^2I^2 + NaI + C^2H^4O.$$

According to more recent experiments by Butlerow (*ibid.* cxiv. 204; cxviii. 325) it appears that acrylic acid, $C^3H^4O^2$, and ethyl-lactic acid, $C^5H^{10}O^3$, are likewise formed in this reaction.

14. Iodoform heated with *potassium* produces a violent explosion.

15. With *triethyl-phosphine*, iodoform unites directly, without the aid of heat, yielding the tri-iodide of formyl-nonethyl-triphosphonium (Hofmann, Proc. Roy. Soc. x. 189)·

$$CHI^3 + 3(C^2H^5)^3P = C^{19}H^{46}P^3I^3 = [(CH)'''(C^2H^5)^9P^3]'''I^3.$$

IODOLITE. A meteoric mineral mentioned by C. U. Shepard among a number of others which have been but imperfectly described. (Sill. Am. J. [2] ii. 377; vi. 402; xv. 363.)

IODOMECONE. $C^3H^4I^8O^3$. (J. Brown, Edinb. Phil. Trans. xxi. [1] 49.)—A substance formed by treating pyromeconic acid with excess of protochloride of iodine:

$$C^5H^4O^3 + 8ICl + 4H^2O = C^3H^4I^8O^3 + 2CO^2 + 8HCl.$$

On adding potash to the yellow liquid thus obtained (after separation of a small quantity of iodopyromeconic acid) impure iodomecone is obtained as a black precipitate which redissolves on agitation. The addition of potash must be discontinued as soon as this precipitate exhibits a lighter colour, no longer redissolves on agitation, and is not increased by fresh additions; and by then collecting the precipitate, and washing it with cold water, and repeatedly crystallising it from boiling alcohol, iodomecone is obtained in the pure state. It may be obtained in the same manner from meconic or comenic acid, which differ from pyromeconic acid only by the elements of carbonic anhydride.

Iodomecone forms shining yellow hexagonal plates, having an odour which recalls that of saffron; it has neither an acid nor an alkaline reaction, sublimes below 100°; is insoluble in water, soluble in alcohol and in ether, insoluble in hydrochloric acid, which does not decompose it even at the boiling heat. It is decomposed by strong nitric acid, and with aid of heat by strong sulphuric acid. Caustic potash, after long boiling, abstracts from it a small portion of iodine.

IODOMECONIN. See Meconin.

IODOMELANILINE. See Melaniline.

IODOMERCURATES. Compounds of mercuric iodide with the more basic iodides. (See Mercury, Iodides of.)

IODOMETHYLAMINE. See Methylamine.

IODOMETHYL-SELENIOUS ACID. See Selenious Ethers.

IODOMORPHINE. See Morphine.

IODONICOTINE. See Nicotine.

IODONITROHARMINE. Syn. with Di-iodide of Nitroharmine (p. 11).

IODONITROPHENIC ACID. See Phenic acid, Derivatives of.

IODOPAPAVERINE. See Papaverine.

IODOPHENYLAMINE. See Phenylamine, Derivatives of.

IODOPHENYLCITRACONIMIDE. See Citraconic acid, Amides of (i. 993).

IODOPIANYL. Syn. with Iodomeconin.

IODOPLATINATES. Compounds of platinic iodide with the more basic iodides. (See Platinum, Iodides of.)

IODOPROPYLENE. See Allyl, Iodides of (i. 142).

IODOPYRITE. Syn. with Iodite.

IODOPYROMECONIC ACID. See Pyromeconic acid.

IODOQUININE. See Quinine.

IODOSALICYLIC ACID. See Salicylic acid.

IODOSTRYCHNINE. See STRYCHNINE.

IODO-SUBSTITUTION COMPOUNDS. Iodine, though generally speaking very similar in its action to chlorine and bromine, acts for the most part less energetically, and is much less disposed to form substitution-compounds by direct action. Some compounds containing hydrogen, indeed, are acted upon by iodine in the same manner as by bromine or chlorine, part of the hydrogen being abstracted to form hydriodic acid, and its place being supplied by an equivalent quantity of iodine; such is the case with ammonia (iii. 280), ethylamine (ii. 536), methylamine, and phenylamine. But iodated organic acids cannot, for the most part, be formed in this way; to produce them from the original acids it is necessary to use chloride of iodine instead of free iodine, so that the superior affinity of the chlorine for hydrogen may remove it, and enable the iodine to take its place (p. 294) *e. g.*:

$$\underset{\text{Pyromeconic acid.}}{C^5H^4O^3} + ICl = HCl + \underset{\text{Iodopyromeconic acid.}}{C^5H^3IO^3}.$$

On the other hand, **Kekulé** (Chem. Soc. J. xvii. 206) has lately shown that many iodo-substitution compounds are decomposed by hydriodic acid, iodine being set free and the original acid reproduced, *e. g.*:

$$\underset{\text{Iodopropionic acid.}}{C^3H^5IO^2} + HI = \underset{\text{Propionic acid.}}{C^3H^6O^2} + I^2.$$

It is evident that where this reaction takes place, it is impossible that an iodised compound can be produced by the direct action of iodine on an organic acid. [For an exception, perhaps only apparent, to this rule, see SALICYLIC ACID.]

The action of hydriodic acid on iodated organic compounds just noticed explains the reducing action which it exerts on certain organic acids (p. 285). The reaction takes place in two stages, an iodo-substitution compound being first formed, and subsequently decomposed in the manner above explained. *e. g.*:

$$\underset{\text{Glycollic acid.}}{C^2H^4O^3} + HI = H^2O + \underset{\text{Iodacetic acid.}}{C^2H^3IO^2}.$$

$$\underset{\text{Iodacetic acid.}}{C^2H^3IO^2} + HI = I^2 + \underset{\text{Acetic acid.}}{C^2H^4O^2}.$$

IODOSULPHIDE OF ANTIMONY. See ANTIMONY (i. 338).

IODOTELLURATES. See TELLURIUM, IODIDE OF.

IODOTOLUYLIC ACID. See TOLUYLIC ACID.

IOLITE. Syn. with DICHROÏTE (ii. 320).

IONNAPHTHIN. This name is given by **Carey Lea** (Sill. Am. J. [2] xxxii. 211) to a colouring matter obtained in preparing naphthylamine from nitronaphthylene by the action of ferrous acetate (*Gmelin's Handbook*, xiv. 95, 5). If the mixture is heated before being treated with caustic potash, a faint red-coloured liquid distils over, which turns violet on addition of mineral acids, and if subsequently heated, assumes a dark purple-blue colour, and after a while yields a black crystalline precipitate, the quantity of which is increased by further heating; this is ionnaphthin. The crystals are black, with green metallic reflex, and dissolve in alcohol with blood-red colour, which, on addition of a very small quantity of sulphuric or nitric acid, changes to scarlet, and finally to purple-blue, is not altered by heating with sulphuric acid, but is changed to straw-yellow by hot nitric acid. From the brown mother-liquor, ammonia throws down dark-coloured flocks, which are insoluble in water and in alcohol, are blackened by dilute sulphuric acid and bichromate of potash, and then form a violet solution with dilute nitric acid.

IPECACUANHA. An emetic substance, the root of several plants growing in South America. All the kinds have nearly the same ingredients, but differ in the amount of the active principle (*emetin*) which they contain. The best is the annulated, yielded by *Cephalis Ipecacuanha*, a small shrubby plant of the rubiaceous order, native of Brazil and New Granada. It is found in commerce in pieces from 2 to 6 inches long and about the thickness of a straw, much bent or twisted, and sometimes branched, with a remarkably knotty character, owing to numerous circular depressions or clefts, which give the whole the appearance of a number of rings. It consists of a central axis called *meditullium*, and an external portion called the *cortical part*. Each of these contains emetin, but by far the greater portion exists in the cortical part.

The following are analyses of different kinds of ipecacuanha:

	a	b		c
		Cortical part.	Meditullium.	
Fatty matter	1·2	2	trace	2
Wax		6		
Resin	1·2			
Emetin	16·0	16	1·15	14
Non-emetic extract	. .	. .	2·45	
Gum	2·4	10	5·00	16
Albumin	2·4			
Starch	53·0	42	20·00	18
Woody fibre	12·5	20	66·40	48
Gallic acid?	trace			
Loss	11·3	4	5·00	2
	100·0	100	100·00	100

a. Grey ipecacuanha, analysed by Barruch and Richard (the 2·4 per cent. gum includes saline matters). *b.* Blackish-grey, analysed by Pelletier. *c.* Reddish-grey, deprived of its meditullium, analysed by Pelletier. In an ash-grey variety, Pelletier found 9 per cent. fatty matter, 12 emetin, and 79 starch, gum, and woody fibre.

Another sort of ipecacuanha is obtained from the *Psychotria emetica.* This kind contains only 9 per cent. emetin; and the undulated or amylaceous ipecacuanha, the produce of *Richardsonia scabra*, contains only 6 per cent. emetin, with 92 per cent. starch. Besides these, the roots of numerous other plants are used in tropical countries as emetics, and often termed ipecacuanha. (Pelouze et Frémy, *Traité*, vi. 399.—*Penny Cyclopædia*, xiii. 17.—Rochleder, *Phytochemie*, s. 131.)

IPECUANIC ACID. An acid existing, according to Willigk (Ann. Ch. Pharm. lxxvi. 342), in the root of *Cephalis Ipecacuanha.* It is extracted from the root by boiling with alcohol, precipitating with basic acetate of lead, and decomposing the lead-salt with sulphydric acid. It is a reddish-brown, very bitter, amorphous mass, soluble in ether, more soluble in alcohol and water. It colours ferric salts green, the colour being changed to violet by ammonia. Its dilute solution does not precipitate neutral acetate of lead. When mixed with an alkali, it absorbs oxygen from the air and becomes coloured. It gives by analysis 56·22 per cent. C, and 6·23 H, whence Willigk deduces the formula $C^{14}H^{18}O^{7}$. Pelletier (Ann. Ch. Phys. iv. 172) regarded it as gallic acid.

IPOMÆIC ACID. An acid produced by the action of nitric acid on rhodeoretic acid, a derivative of jalap-resin (*q. v.*) It agrees with sebacic acid in all its properties excepting its melting point—which is 104°, whereas sebacic acid melts at 127°—and in some of its relations to bases (Mayer, Ann. Ch. Pharm. lxxxiii. 143). See SEBACIC ACID.

IRIDIUM. Ir = 99·13 or Irr = 198·26.—The black scales which remain when native platinum is dissolved in nitromuriatic acid were found by Smithson Tennant (Phil. Trans. 1804) to consist of an alloy of two metals, iridium and osmium, hence called iridosmine. The same alloy occurs in flat white metallic grains in native platinum. Iridium has also been observed in combination with about 20 per cent. of platinum, crystallised in octahedrons, which are whiter than platinum, and are said to have a greater density, namely 22·66.

The separation of the osmium and iridium is effected by the following methods:—

1. The iridosmine is mixed with an equal weight of common salt, and subjected to the action of a stream of chlorine in a porcelain tube heated to redness. Double chlorides of iridium and sodium, and of osmium and sodium, are then formed, and if the chlorine is moist, a certain quantity of osmic acid, which volatilises, and may be condensed in aqueous ammonia. The mixture of the double chlorides is detached from the tube and boiled with nitric acid. Osmic acid is then evolved, and may be condensed in an alkaline solution, while the chloride of sodium and iridium remains in the solution, and, when mixed with sal-ammoniac, yields a precipitate of chloride of iridium and ammonium, which, on ignition, leaves metallic iridium. (Wöhler, Pogg. Ann. xxxi. 161.)

2. A mixture of 100 grms. of iridosmine and 300 grms. of nitre is placed in an earthen crucible, and heated to bright redness for an hour, the resulting mixture of osmate and iridiate of potassium poured out on a cold metal plate, then introduced into a tubulated retort, and distilled with a large excess of nitric acid. A large quantity of

osmic acid then volatilises and condenses in the receiver in beautiful white crystals. As soon as the evolution of osmic acid ceases, water is added, and the residue, consisting of oxide of iridium, with a certain quantity of oxide of osmium, is collected on a filter and boiled with nitromuriatic acid, which dissolves the two metals as chlorides. The solution is then mixed with sal-ammoniac, which precipitates chlorosmate and chloriridiate of ammonium; and the mixed precipitate is suspended in water and exposed to a current of sulphurous acid, whereby the chloriridiate of ammonium, NH^4IrCl^3, is converted into chloriridite, $(NH^4)^3Ir^2Cl^6$, which dissolves, while the chlorosmate of ammonium remains unaltered, and does not dissolve: this latter chloride yields pure metallic osmium by calcination. The solution of chloriridiate of ammonium leaves, when evaporated, beautiful brown crystals, which by calcination yield metallic iridium. (Frémy, Compt. rend. xviii. 144.)

Iridosmine generally, however, contains platinum as well as other metals of the same group, which are not effectually separated by the methods just described. The complete separation of the several metals of the platinum group has of late years formed the subject of several elaborate investigations, which will be more fully considered under PLATINUM; those more especially relating to iridium are the following:

3. The separation of iridium from platinum depends upon the ready convertibility of the chloriridiate of ammonium or potassium to a lower degree of chlorination by the action of reducing agents, and the easy solubility of the resulting double chloride. Mucklé and Wöhler (Ann. Ch. Pharm. civ. 368) treat chloriridiate of ammonium containing platinum with solution of cyanide of potassium, adding the solution cautiously and avoiding an excess, then digest it at a gentle heat till the undissolved portion has acquired a light yellow-brown colour. The chloriridiate of ammonium is thus converted into chloriridite of potassium, which easily dissolves, whereas the chloroplatinate resists the action of the reducing agent much longer, and remains undissolved. The completion of the process is plainly indicated by the change of colour of the undissolved salt, since the presence of a small quantity of the iridium-salt gives a deep red colour to the chloroplatinate.

The separation may also be effected by sulphocyanate of potassium, the action of which is similar to that of the cyanide, but somewhat more complex. It is better, however to reduce the chloriridiate of ammonium by sulphydric acid, or by sulphurous acid, as in Frémy's method (see above), because metallic iridium may then be immediately obtained by simply evaporating the filtered solution of the chloriridite of ammonium, and igniting the residue. (Claus, Ann. Ch. Pharm. cvii. 129; Jahresb. 1858, p. 210.)

4. The iridosmine which remains after the complete exhaustion of platinum ore with nitromuriatic acid is a mixture of two substances, one of which is scaly and consists of osmium, iridium, and ruthenium, while the other, which is granular, contains but mere traces of osmium and ruthenium, but is very rich in iridium and rhodium. Now when this residue is heated to bright redness in a porcelain tube through which a current of air (freed from carbonic acid by passing through potash, and from organic matter by passing through oil of vitriol) is drawn by means of an aspirator, osmic acid and oxide of ruthenium are formed, the latter crystallising in the colder part of the tube, while the more volatile osmic acid is carried forwards (see OSMIUM and RUTHENIUM), and an alloy of iridium and rhodium remains behind. To separate these metals, the residue thus obtained is calcined in an earthen crucible with four times its weight of nitre, care being taken not to carry the process too far; and the product is exhausted with boiling water and filtered. The filtrate consists of an alkaline solution of osmite of potassium, the osmium never being completely removed by the previous roasting, while a copious precipitate containing the iridium and rhodium, together with potash, remains on the filter. On treating this precipitate with nitromuriatic acid for several hours, the iridium is converted into chloriridiate of potassium, which may be dissolved out by boiling water, the rhodium still remaining undissolved. (Frémy, Compt. rend. xxxviii. 1008.)

5. Iridosmine in fine powder (into which state it may be brought by calcining it in a crucible with four or five times its weight of zinc, till the flame no longer exhibits any trace of that metal) is mixed with 3 pts. peroxide and 1 pt. of nitrate of barium, and heated to redness for an hour. The black friable substance remaining in the crucible, and consisting of osmo-iridiate of barium containing ruthenium, is freed from osmic acid by prolonged boiling with nitromuriatic acid; the baryta is then precipitated by the exact quantity of sulphuric acid required (this quantity being known from the previous weighings); the dark red filtrate mixed with excess of hydrochloric acid is evaporated over the water-bath, and mixed, towards the end of the operation, with a large excess of solid sal-ammoniac; the residue, no longer smelling of acid, is washed, first with a concentrated solution of sal-ammoniac (which dissolves out the rhodium, together with metals not belonging to the platinum group) till the liquid no longer

runs away coloured, then with a more dilute solution of the same salt; the residue, chiefly consisting of chloriridiate of ammonium, is dried, heated to commencing redness (so as to decompose the ammonium-salts completely, the chlorides of the platinum metals imperfectly), then in a current of hydrogen to complete the reduction; and the resulting metallic sponge, in which the metals are not alloyed, but only mechanically mixed, is treated with nitromuriatic acid, which completely removes any platinum that may still be present, but leaves behind a certain quantity of osmium. The remaining pulverulent metallic mass is then fused with a mixture of nitrate and hydrate of potassium; and the unattacked portion of the metal, after being carefully freed from rutheniate of potassium by washing with water, is heated to whiteness in a crucible lined with charcoal, in which it bakes together; then placed in a vessel of lime and ignited in an oxy-hydrogen flame containing excess of oxygen, till every trace of the odour of osmium has disappeared; and lastly, fused at the strongest heat which the oxy-hydrogen flame is capable of producing. (Deville and Debray, Ann. Ch. Phys. [3] lvi. 385; Rép. Chim. pure, 1859, p. 541; Jahresber. 1859, p. 241.)

6. An intimate mixture of 100 pts. iridosmine or platinum-residues, 100 pts. nitrate of barium and 200 pts. caustic baryta, is heated in a red-hot earthen crucible; and the fritted mass, after being pulverised, is thrown by small portions into cold water, then mixed with nitric acid, and heated till all the osmium is driven off as osmic acid. A small quantity of hydrochloric acid is then added; the liquid is heated and filtered through gun-cotton; and the iridium is separated from the other metals contained in it, as in the preceding method. (Deville and Debray, Compt. rend. liv. 1138.)

7. Platinum-residue, finely pulverised and freed by levigation from the coarser grains of osmide of iridium, is gently ignited in a covered crucible, then mixed with 1 pt. finely granulated lead and 1½ pt. litharge, and heated, with stirring, in a thick-bottomed hessian crucible till the mixture becomes perfectly fluid. By this means all the silicates and earthy minerals present are converted into a slag; the metals more oxidable than lead are oxidised; and the specifically heavier platinum-metals collect in the lead-regulus. The latter, after being freed from slag, is dissolved at a gentle heat in nitric acid diluted with 1½ vol. water, which dissolves principally copper and palladium, leaving a residue which, when washed by decantation, consists of a fine black metallic powder of iridium, rhodium, and ruthenium, together with fine grains and scales of iridosmine, which must be separated by levigation. The black powder is immediately available for further treatment; the iridosmine, on the other hand (together with the coarser grains obtained by levigating the crude platinum-residue), is reduced to powder by fusing it in a charcoal crucible with twice its weight of granulated zinc, and then raising the heat to whiteness to drive off the zinc (p. 315). The finely divided iridosmine, is then heated in a stream of oxygen to expel the osmium, and the residue, together with the black powder of iridium, rhodium, and ruthenium above-mentioned, is mixed with an equal weight of chloride of sodium, and decomposed by Wöhler's method with chlorine gas (p. 314). The dark brown solution thus obtained is mixed with a little hydrochloric acid and one-fourth of its bulk of ordinary nitric acid, and distilled to one-third, the osmic acid which passes over being condensed by ammonia; the remaining liquid, which contains the double chlorides of iridium, &c., is mixed, while still warm, with an equal volume of a saturated solution of sal-ammoniac; and the red-brown precipitate, after standing for some days, is separated from the liquid, and washed with sal-ammoniac solution till the liquid runs off colourless. The wash-water contains the whole of the rhodium-salt, the mother-liquor consists chiefly of chloride of iron and ammonium, with traces of iridium, rhodium, and gold. The precipitate, consisting of chloriridiate of ammonium contaminated with platinum and ruthenium-salt, is mixed, after drying, with 1½ pt. cyanide of potassium, and melted for 10 or 15 minutes in a capacious porcelain crucible; the cooled mass is dissolved in the smallest possible quantity of water; and the yellow filtrate (after the whole of the free cyanide of potassium has been decomposed by dilute hydrochloric acid) is precipitated by sulphate of copper. The resulting precipitate, consisting chiefly of platino- and iridio-cyanide of copper, is washed with boiling water, first by decantation, then on a filter, and finally decomposed with boiling baryta-water, whereby oxide of copper is separated, and the platinum and iridium are converted into platino- and iridio-cyanides of barium, which are easy to separate, the platinum-salt, which is much more soluble in hot than in cold water, separating out completely at first, and the white iridium-salt crystallising afterwards. The mother-liquor of the iridium-salt contains a small quantity of ruthenio-cyanide of potassium; any rhodium-salt that may be present may be precipitated by acetic acid. (C. A. Martius, Ann. Ch. Pharm. cxvii. 357; Jahresber. 1860, p. 202.)

8. The following process is given by Deville and Debray (Ann. Ch. Phys. [3] lxi. 5; Jahresb. 1861, p. 889) for obtaining iridium, pure or alloyed, from the substance

known in the Russian mint as "iridium-oxide"—a not quite uniform mixture containing iridium as oxide, and having the following average composition:

Volatile substances (and oxygen)	28·0
Soluble salts (NaCl and Ca^2SO^4)	12·0
Platinum	3·8
Rhodium	1·8
Palladium	0·4
Copper	0·6
Iron	0·7
Iridium (and loss)	52·7
	100·0

The substance is ignited in a crucible lined with charcoal; and the residue is washed with water, heated with strong sulphuric acid to the boiling point of that liquid, and again washed with water, whereby all the soluble salts are removed, together with the copper and iron. If the amount of platinum is known, and the object is to prepare an alloy, the washed metal is heated to whiteness (to give it a compact texture), and then fused before the oxy-hydrogen blowpipe. To obtain pure iridium, the crude metallic powder, after treatment with sulphuric acid, is digested with nitromuriatic acid, the greater part of the iridium (with traces of rhodium) then remaining behind.

Metallic iridium is obtained from the chloride by reducing that salt with hydrogen at a red heat, or by exposing it alone to a very high temperature, or more easily by igniting the chloriridiate of ammonium (p. 314), in the form of a grey metallic powder much resembling spongy platinum. It is the most refractory of all bodies excepting ruthenium and osmium; not being fusible in the flame of the ordinary oxy-hydrogen blowpipe. Children, however, by the discharge of a very large voltaic battery, succeeded in melting it into a globule which was white and very brilliant, but still a little porous, and had a density of 18·68; and Deville and Debray, by means of their powerful oxy-hydrogen blast furnace, have fused it completely into a pure white mass, resembling polished steel, brittle in the cold, somewhat malleable at a red heat, and having a density equal to that of platinum, viz. 21·15. By moistening the pulverulent metal with a small quantity of water, pressing it tightly, first between filtering paper, then very forcibly in a press, and calcining it at a white heat in a forge-fire, it may be obtained in the form of a compact, very hard mass, capable of taking a good polish, but still very porous, and of a density not exceeding 16·0. After strong ignition it is insoluble in all acids, but when reduced by hydrogen at low temperatures, it oxidises slowly at a red heat, and dissolves in nitromuriatic acid. It is usually rendered soluble by fusing it with nitre and caustic potash, or by mixing it with common salt, or better with a mixture of the chlorides of potassium and sodium, and igniting it in a current of chlorine, thereby it is converted into the soluble chloriridiate of potassium or sodium.

IRIDIUM, ALLOYS OF. 1 pt. of iridium combines at a white heat with 4 pts. of copper, forming a ductile, pale red alloy, which is much harder than copper, and gives up its copper to nitric acid, the iridium remaining in the form of a black powder.

With gold, iridium forms a malleable alloy, having a colour very much like that of gold: nitromuriatic acid dissolves out the gold and leaves the iridium.

1 pt. of iridium and 8 pts. lead heated together to an intense red heat, form an alloy which is very ductile, but much harder and whiter than lead, and behaves with nitric acid like the copper alloy. On cupellation, the iridium is left as a soft black powder.

With mercury, iridium forms a viscid amalgam, which is obtained by immersing sodium-amalgam in an aqueous solution of chloriridiate of sodium. When very strongly ignited, it leaves a black powder, from which boiling nitric acid extracts a small quantity of mercury, leaving a residue of pure iridium, soluble in boiling nitromuriatic acid. (Böttger, J. pr. Chem. xii. 252.)

The compound of iridium and osmium is not, properly speaking, an alloy, inasmuch as osmium is rather a metalloïd than a metal. (See IRIDOSMINE.)

Platinum and iridium easily melt together, and form alloys which, even when they contain 20 per cent. of iridium, are still malleable and capable of being worked, but are less easily attacked by chemical reagents than pure platinum. (Deville and Debray.)

Equal weights of the two metals form a brittle alloy capable of welding to a certain extent. The alloy of platinum with a few parts per cent. of iridium is ductile and much harder than pure platinum, and more capable of resisting the action of fire and of chemical reagents (Berzelius). An alloy made by fusing 1 pt. iridium and 10 platinum in the flame of the oxyhydrogen blowpipe, is very malleable, susceptible of hardening, does not tarnish, and when laid on copper serves for metallic mirrors. (Gaudin, J. pr. Chem. xvi. 55.)

A native alloy of iridium and platinum called native iridium occurs in the Ural in cubo-octahedrons of specific gravity varying from 21·85 to 22·65 and 22·8, and in Brazil in white round grains of specific gravity 16·94. (Svanberg, *Gmelin's Handb.* vi. 393.)

	Pt.	Ir.	Rh.	Pd.	Os.	Fe.	Cu.		
Ural .	19·64	76·85	. . .	0·89	. .	. .	1·78	=	99·16
Brazil .	55·44	27·79	6·86	0·49	trace	4·14	3·30	=	98·02

1 pt. of iridium unites but imperfectly with 2 pts. of silver. (Vauquelin.)

1 pt. of iridium unites with 4 pts. of tin at an intense red heat, forming a dull white easily crystallisable, hard, malleable alloy. (Vauquelin.)

When iridosmine is fused with from 5 to 6 times its weight of tin, the alloy being kept for a long time at a red heat in the charcoal crucible, then slowly cooled and treated with hydrochloric acid, tin passes into solution, together with traces of iridium, and there remains a mixture (separable by a fine sieve) of finely pulverulent crystalline osmium, and large shining cubic crystals of an alloy of tin and iridium, which is not attacked by nitromuriatic acid, but when strongly ignited in an atmosphere of sulphydric acid, gives off the whole of the tin, amounting to 56·6 per cent., as sulphide, leaving 43·4 per cent. iridium.—By fusing tin with a mass containing platinum, iridium, and rhodium, and dissolving the excess of tin in hydrochloric acid, a crystalline residue is obtained, whose composition (if Pt denotes the platinum metals in general) is Pt^2Sn^3 or $PptSn^3$. (Deville and Debray.)

An alloy of iridium and zinc, obtained as in Deville and Debray's first method of preparing an alloy of iridium and tin, is not crystallisable.

IRIDIUM, CARBIDE OF. When a coherent mass of iridium is held in the flame of a spirit-lamp, black masses appear on its surface, which are a carbide containing 19·83 per cent. carbon, or IrC^2. The carbon burns off readily in the air.

IRIDIUM, CHLORIDES OF. Iridium appears to form four compounds with chlorine; but only two of them have been obtained in definite form.

The *protochloride*, IrCl, is said by Berzelius to be formed when pulverised iridium is heated to low redness in chlorine gas. It is described as a dark olive-green powder, insoluble in water, slightly soluble in hydrochloric acid, and forming double salts with the chlorides of the alkali-metals. According to Claus, however (Ann. Ch. Pharm. lix. 255), the so-called protochloride of iridium is merely a mixture of the sesquichloride with metallic iridium. The protochloride appears, however, to exist in certain double salts (p. 322).

The *sesquichloride*, Ir^2Cl^3 (or *trichloride*, $IrrCl^3$), is prepared by dissolving the sesquioxide in hydrochloric acid, and evaporating; it also sublimes when iridium, either alone or mixed with nitre, is ignited in chlorine gas. It is black, deliquescent, and does not crystallise. It unites with the chlorides of the alkali-metals, forming double salts, called chloro-iridites, which are prepared, either by mixing the solutions of the component chlorides in the required proportions, and evaporating, or by reducing the solutions of the corresponding chloriridiates with sulphurous acid, sulphydric acid, alcohol, or ferrocyanide of potassium. Claus has obtained the compounds $3NH^4Cl.Ir^2Cl^3.3H^2O$, $3KCl.Ir^2Cl^3.3H^2O$, and $3NaCl.Ir^2.Cl^3.12H^2O$. They are olive-green, pulverulent salts, soluble in water; the sodium-salt is also soluble in alcohol; the other two are insoluble in alcohol. Berzelius obtained a potassium-salt containing $2KCl.Ir^2Cl^3$.

Chloriridite of silver, $Ag^3Ir^2Cl^6 = 3AgCl.Ir^2Cl^3$, is produced, on adding nitrate of silver to aqueous chloriridiate of potassium, as a deep indigo-coloured flocculent precipitate, which, however, becomes paler in a few seconds, and finally loses its colour altogether. The reaction, which is attended with evolution of oxygen, is:

$$6AgNO^3 + 4KIrCl^3 + H^2O = 2Ag^3Ir^2Cl^6 + 4KNO^3 + 2HNO^3 + O.$$

With a boiling solution of chloriridiate of potassium, the same compound is formed immediately, without the intermediate production of a blue substance. The silver-salt is insoluble in water and in acids, and but slightly soluble in ammonia. When it is covered with strong aqueous ammonia and left to itself for a few days, one portion dissolves, and the remainder is converted into a crystalline modification of the salt composed of rhombohedrons having an adamantine lustre. (Claus, Ann. Ch. Pharm. lxiii. 338.)

The *dichloride*, $IrCl^2$ (or *tetrachloride*, $IrrCl^4$), is obtained by dissolving very finely divided iridium, or one of its oxides, or the sesquichloride, in nitromuriatic acid, and heating the liquid to the boiling point. On evaporating the solution, it remains in the form of a black, deliquescent, amorphous mass, translucent with dark red colour at the edges. It sustains a rather strong heat without decomposition, but at a higher temperature is reduced to the sesquichloride and ultimately to metallic iridium (Berzelius). It dissolves in water, forming a reddish-yellow solution. It unites with the alkaline chlorides, forming definite crystalline double salts called chloriridiates, the general formula of which is $MIrCl^3 = MCl.IrCl^2$ (or $M^2IrrCl^6 = 2MCl.IrrCl^4$). The *ammonium-salt*, $2(NH^4)IrCl^3.H^2O$ [or $(NH^4)^2IrrCl^6.H^2O$], is obtained, on mixing the solutions of the component chlorides, as a very dark brown precipitate, which dissolves in boiling water and crystallises in octahedrons on cooling. It dissolves in 20 pts. of cold water, forming a dark red-brown liquid, and imparts distinct coloration to 4,000 pts. of water. The red colour often exhibited by chloroplatinate of ammonium is due to small quantities of this salt. The aqueous solution supersaturated with ammonia forms a pale yellow mixture, which becomes perfectly colourless when exposed to light, but afterwards turns purple, then violet, and finally assumes a beautiful blue colour.

The chloriridiates are easily converted by the action of sulphurous acid, sulphydric acid, and other reducing agents into the more soluble chloriridites, a reaction which affords the means of separating iridium from platinum, the chloroplatinates being but very slowly reduced under the same circumstances, and not converted into more soluble salts (p. 315).

The *potassium-salt*, $KIrCl^3$ or K^2IrrCl^6, is precipitated on mixing the aqueous solutions of its component salts. It may also be prepared by passing chlorine gas over a gently ignited and intimate mixture of finely divided iridium and chloride of potassium; filtering from unaltered iridium; dissolving the unfused black-brown mass in hot water; mixing it with nitromuriatic acid; and evaporating to dryness; extracting the excess of chloride of potassium by small quantities of cold water; dissolving the residue in boiling water; adding a small quantity of nitromuriatic acid, and evaporating to the crystallising point. It crystallises in black octahedrons, yielding a red powder. It dissolves very slowly in cold water, but quickly in boiling water, forming a liquid which appears deep red in the mass, but yellow in thin films. It is insoluble in saline solutions and in alcohol, which precipitates it from solution in water. The aqueous solution, mixed with excess of potash, behaves in the same manner as the ammonium-salt with excess of ammonia. At a strong heat, it is converted into chloriridite of potassium, and at a still higher temperature, leaves metallic iridium mixed with chloride of potassium. The *sodium-salt*, $NaIrCl^3.3H^2O$ (or $Na^2IrrCl^6.6H^2O$) is obtained, like the potassium-salt, by passing chlorine over a gently ignited mixture of iridium and chloride of sodium. It forms black tables and four-sided prisms with dihedral summits, isomorphous with the corresponding platinum-salt. When heated, they leave the anhydrous salt in the form of a brownish-grey powder. It is easily soluble in water, and the solution mixed with sal-ammoniac yields a precipitate of chloriridiate of ammonium.

A *trichloride* of iridium was obtained by Berzelius, in combination with chloride of potassium, by fusing iridosmine with nitre, distilling the product with nitromuriatic acid, and treating the residue with successive portions of water. A dark red solution was then obtained, which yielded a salt having the composition $3KCl.IrCl^3$, but according to Claus, the salt thus obtained was really a ruthenium-compound, having been prepared by Berzelius from iridosmine containing ruthenium. Pure iridium fused with nitre and distilled with nitromuriatic acid, yields a salt containing dichloride of iridium.

IRIDIUM, DETECTION AND ESTIMATION. Iridium in its free state is easily distinguished from all other metals, excepting rhodium and ruthenium, by its insolubility in acids, not being attacked in the compact state by any acid whatever, and in the state of fine division, only very slowly by nitromuriatic acid. Its infusibility, even in the ordinary oxy-hydrogen blowpipe flame, serves also to distinguish it from all metals excepting rhodium, ruthenium, and osmium.

It may be distinguished from rhodium by fusing it in the finely divided state with acid sulphate of potassium. The iridium is then converted into sesquioxide, but does not dissolve in the acid sulphate or colour it red, as rhodium does. Another method of distinguishing iridium from rhodium, and likewise from ruthenium, is to mix it intimately with chloride of potassium or sodium, heat the mixture in a stream of chlorine, and dissolve the resulting double chloride in water: iridium thus treated yields a black-brown solution, rhodium a rose-red, and ruthenium an orange-yellow solution. (See RHODIUM and RUTHENIUM.)

All compounds of iridium are easily reduced to the metallic state by ignition in an atmosphere of hydrogen; the reduced metal may then be tested in the manner just described.

Iridic solutions (containing the dioxide or dichloride) which are those of most frequent occurrence, are of a dark brown-red colour; iridous solutions (containing the sesquioxide or sesquichloride) have an olive-green colour. The characters of an iridic solution are best observed with chloriridiate of sodium, as all the other compounds are but very slightly soluble.

Caustic *potash* in excess decolorises the solution of an iridic salt, changing the dark red colour to a very faint greenish tint, and after some time throws down a slight black-brown precipitate of chloriridiate of potassium. If the clear solution be heated, and then left in contact with the air, it first acquires a faint red and then a blue colour, gradually increasing in intensity from the surface downwards, and ultimately becoming as deep as that of an ammoniacal solution of copper. The solution evaporated to dryness, leaves a white mass, which, when treated with water, yields a colourless solution and an insoluble blue powder consisting, according to Claus, of iridic hydrate. This is the most characteristic of all the reactions of iridium. The presence of *palladium* interferes, however, with the production of the blue colour, and gives rise to the precipitation of iridic oxide. A solution of iridium containing *platinum* is likewise not coloured blue by potash, but is decolorised, and yields a red precipitate of chloroplatinate of potassium containing iridium; on heating the liquid, this precipitate redissolves, and another precipitate is formed consisting of platiniferous iridic oxides. If the solution contains *rhodium*, no alteration takes place at first; but subsequently, a light yellow precipitate of rhodic hydrate is produced; or if the solution is hot, the precipitate is of a dirty greyish-green colour, and the solution becomes colourless.

Ammonia in excess also decolorises iridic solutions, and forms a slight blackish precipitate. On boiling the solution for some time, till the greater part of the ammonia is expelled, the solution acquires a blue colour, especially if left exposed to the air; but the colour is neither so pure nor so deep as that produced by potash. The presence of palladium, platinum, or rhodium modifies the reaction with ammonia much in the same manner as with potash. *Carbonate of potassium* forms a red-brown precipitate, which gradually dissolves, the liquid afterwards turning blue when exposed to the air. *Carbonate of ammonium* imparts a blue colour to the liquid under the influence of the air. *Sulphydric acid* decolorises the solution at first, and afterwards forms a brown precipitate. *Chloride of ammonium* forms a dark cherry-red, pulverulent precipitate of chloriridiate of ammonium. *Ferrocyanide of potassium* and *protosulphate of iron* decolorise the solution. *Dichloride of tin* forms a light brown precipitate. *Zinc* precipitates metallic iridium as a black powder.

Quantitative estimation and separation.—Iridium is completely precipitated from the solution of an iridic salt by treating the solution with chloride of ammonium or chloride of potassium, and then adding alcohol containing ether, in which the chloriridiate of ammonium or potassium is quite insoluble. The precipitate may be collected on a weighed filter, washed with alcohol and ether, dried in the water-bath, and then weighed. The ammonium-precipitate contains 44·21 per cent., the potassium-precipitate 40·38 per cent. iridium. The ammonium-precipitate may also, after washing with ether-alcohol (not on a weighed filter), and drying, be carefully ignited in a tared platinum crucible, and the weight of the remaining iridium directly determined.

If the iridium exists in solution as sesquichloride, it must, before precipitation, be converted into dichloride by passing chlorine gas into it, or heating it with nitromuriatic acid.

The mode of precipitation just described serves for the separation of iridium from al lmetals excepting platinum, rhodium, ruthenium, and osmium; and from all these, except rhodium, it may be separated by reducing it to the state of sesquichloride, and then adding to the liquid an excess of a concentrated solution of sal-ammoniac. Chloriridite of ammonium, $3NH^4Cl.Ir^2Cl^3$, is then formed, which is soluble in sal-ammoniac, whereas the double compounds of chloride of ammonium with the chlorides of the other platinum-metals (except sesquichloride of rhodium) are insoluble in excess of chloride of ammonium.

The reduction of dichloride of iridium in solution to sesquichloride may be effected by any of the reducing agents already mentioned (pp. 315, 319), but the most convenient for analytical purposes is *sulphydric acid.*

When, for example, iridium is to be separated from platinum, both being in the form of dichlorides, the mixture of these compounds, or rather their double salts with chloride of ammonium or potassium, may be treated with a small quantity of water, and solution of sulphydric acid added by small portions. The reduction of the iridic chloride then takes place immediately, a green liquid being formed, rendered milky by precipitated sulphur, and coloured brown by sulphide of platinum, if that metal is present in rather large proportion. Iridium is not precipitated from its solutions as sulphide by sulphydric acid at ordinary temperatures, unless the reagent is added in very large excess, and even then the precipitation takes at least 24 hours. The reduction of the iridium to sesquichloride being complete, sal-ammoniac is added in excess, and the liquid filtered. The platinum then remains undissolved, while the iridium passes into the filtrate, and may be reconverted into dichloride by means of nitromuriatic acid, and precipitated as already described.

The same method may serve to separate iridium from osmium, but the separation of that metal from the other members of the group is generally effected by distillation with nitromuriatic acid, or by roasting in an atmosphere of oxygen. (See OSMIUM.)

Palladium is easily separated from iridium by precipitation with cyanide of mercury, which does not throw down iridium; also by fusion with acid sulphate of potassium, which dissolves the palladium, but merely oxidises the iridium.

The separation of iridium from rhodium may be effected, when the former is in the state of dichloride and the latter in the state of sesquichloride, by treating the solution with excess of chloride of ammonium, which forms, with sesquichloride of rhodium, a double salt soluble in excess of chloride of ammonium, whereas chloriridiate of ammonium is insoluble in excess of that salt. Another mode of separation is founded on the fact that chloriridiate of sodium is soluble, and chlororhodiate of sodium insoluble, in alcohol. The method of fusion with acid sulphate of potassium, whereby rhodium is dissolved while iridium is merely oxidised, serves for the qualitative distinction between the two metals (p. 319), but is not adapted for quantitative separation, because the solution of the rhodium takes place but slowly, and when a small quantity of it is mixed with a considerable quantity of iridium, not a trace of it is taken up by the fused acid sulphate. (See RHODIUM.)

Atomic Weight of Iridium.—The only known determination of this number is that made in 1828 by Berzelius (Pogg. Ann. xiii. 435), and founded on the analysis of chloriridiate of potassium, $KCl.IrCl^2$. 100 parts of this salt ignited in a stream of hydrogen lost 29 pts. of chlorine. Now, as only 2 at. chlorine are given off, the chloride of potassium not being decomposed, we have, for determining the atomic weight of iridium (taking K = 39·2 and Cl = 35·5), the proportion

$$145{\cdot}7 + Ir : 71 = 100 : 29$$

whence

$$Ir = 99{\cdot}13.$$

If the chloriridiate of potassium be supposed to contain tetrachloride of iridium, its formula being $2KCl.IrrCl^4$, then Irr = 198·26.

IRIDIUM, IODIDES OF. (Oppler, *Ueber die Jodverbindungen des Iridiums* (Dissertation), Göttingen, 1857; Jahresb. 1857, p. 263.)—Iridium appears to form three compounds with iodine, namely, IrI, Ir^2I^3, and IrI^2.

The *proto-iodide*, IrI (or di-iodide, $IrrI^2$), or *Hypo-iridious iodide*, appears to be formed, as a brown powder, by passing sulphurous acid gas into water in which iridic iodide is suspended. By dissolving finely pulverised chloriridiate of ammonium in a boiling concentrated solution of iodide of potassium, and leaving the liquid to stand for a few hours, *hypo-iodiridite of ammonium*, NH^4IrI^2 or $NH^4I.IrI$, separates as a black crystalline powder or in blackish-grey spangles.

The *sesqui-iodide*, Ir^2I^3 (or tri-iodide, $IrrI^3$), or *Iridious iodide*, separates as a black crystalline precipitate on adding chloride of ammonium to aqueous iodiridiate of potassium, $KIrI^3$ (iodiridiate of ammonium being probably formed in the first instance, and subsequently resolved into sesqui-iodide of iridium, iodide of ammonium, and free iodine). It is very sparingly soluble in cold water, somewhat more freely in hot water, insoluble in alcohol. It unites with alkaline iodides, forming double salts which may be called iodiridites. The *ammonium-salt*, $2(NH^4)^3Ir^2I^6.H^2O$ (or $2(NH^4)^3IrrI^6.H^2O$) separates in crystalline needles from the mother-liquor of hypo-iodiridite of ammonium (see above) on repeated concentration, first together with the latter, afterwards alone. The *potassium-salt*, $K^3Ir^2I^6$, separates on adding a concentrated solution of iodide of potassium to a solution of sesquichloride of iridium, as a fine crystalline powder, having a green lustre, insoluble in water and in alcohol, dissolving slowly in acids, easily in alkalis when heated. The *silver-salt*, $Ag^3Ir^2I^6$, is obtained on adding nitrate of silver to a solution of iod-iridiate of potassium, as a dark green amorphous precipitate, which afterwards turns brown. The reaction by which it is formed is similar to that of nitrate of silver on chloriridiate of potassium (p. 318).

The *di-iodide*, $IrrI^2$ (or tetra-iodide, $IrrI^4$), or *Iridic iodide*, is obtained as a soft black powder by adding iodide of potassium to a strong solution of dichloride of iridium, and boiling the brown-red liquid, mixed with a little hydrochloric acid. With alkaline chlorides it forms the iodiridiates. The *ammonium-salt*, NH^4IrCl^3, or $(NH^4)^2IrrI^6$, separates after some weeks from a solution of chloriridiate of ammonium in cold concentrated aqueous iodide of potassium, in dark brown shining crystals easily decomposed by heat. The aqueous solution, when gently heated, becomes turbid and black-brown, depositing hypo-iodiridite of ammonium, NH^4IrI^2, and iridic iodide. The *potassium-salt*, $KIrI^3$, or K^2IrrI^6, separates after the iridic iodide itself, from a solution of iridic chloride mixed with iodide of potassium. It is formed also, though in small quantity only, by the action of iodine-vapour on an intimate mixture of iridium and iodide of potassium heated to 60°—70°; and in larger quantity, by adding iridic chloride to a solution of iodide of potassium, the latter being kept in excess; or by dissolving the iridic iodide in iodide of potassium, and leaving the solution to crystallise. It forms dark, metallic-shining, crystalline spangles, appearing as octahedrons under the microscope, easily soluble in water, insoluble in alcohol; it is dissolved by acids, and, with decomposition, by alkalis. The *sodium-salt*, $NaIrI^3$, or Na^2IrrI^6, is obtained on adding a concentrated solution of iodide of sodium to iridic chloride, as a dark brownish-green crystalline powder, insoluble in alcohol and in cold water, sparingly soluble in hot water.

IRIDIUM, OXIDES OF. Iridium forms four compounds with oxygen, namely, Ir^2O, Ir^4O, Ir^2O^2, and Ir^2O^3. The *protoxide*, or *Hypo-iridious oxide*, Ir^2O or $IrrO$, is but little known. It is obtained by precipitating an alkaline hypochloriridite with caustic alkali in an atmosphere of carbonic anhydride (p. 323); but on exposure to the air it is quickly converted into a higher oxide. (Claus.)

The *sesquioxide*, or *Iridious oxide*, Ir^4O^3 or Irr^2O^3, was formerly regarded as the most easily formed and most stable of the oxides of iridium; but, according to Claus, it has a great tendency to take up oxygen and pass to the state of dioxide. It may be prepared by gently igniting a mixture of chloriridite of potassium ($3KCl.Ir^2Cl^3$) with carbonate of sodium in an atmosphere of carbonic anhydride; on treating the product with water, the sesquioxide remains in the form of a black powder insoluble in acids (Claus, Ann. Ch. Pharm. lix. 251). It forms two hydrates, one containing 3 at., the other 5 at. water. The trihydrate, $Ir^4O^3.3H^2O$, is obtained by treating a solution of the olive-green sesquichloride, or one of its double salts, with potash and alcohol, as a black precipitate, which, when treated with hydrochloric acid, yields a small quantity of olive-green sesquichloride. The pentahydrate, $Ir^4O^3.5H^2O$, is obtained by mixing the solution of either of the double salts of sesquichloride of iridium with a small quantity of caustic potash, and leaving the liquid for some time to itself in well-closed and perfectly filled bottles. It is then deposited as a yellowish precipitate with a tinge of olive green; but it cannot be obtained pure, as it easily takes up oxygen, turning blue, and being partially converted into dioxide. It dissolves in the smallest quantity of potash.

Sesquioxide of iridium unites with bases, forming salts which may be called iridites. A solution of a chloriridite in excess of lime-water deposits, after standing for some time out of contact of air, a dirty yellow precipitate containing Ca^3IrO^3 or $3Ca^2O.Ir^2O^3$. (Claus, J. pr. Chem. lxxx. 282; Jahresb. 1860, p. 207.)

The *dioxide*, or *Iridic oxide*, Ir^2O^2 or $IrrO^2$, is, according to Claus, the most easily prepared and most stable of all the oxides of iridium, and is always deposited in the form of a bulky, indigo-coloured hydrate, $Irr^2O^2.2H^2O$, when a solution of either of the chlorides of iridium or their double salts is boiled with an alkali; but it always retains 3 or 4 per cent. of the alkali. The hydrate may also be obtained by dissolving the hydrated sesquioxide in potash and treating the solution with an acid. A greenish-blue precipitate is then formed, which gradually absorbs oxygen from the air and assumes an indigo-colour. The hydrate parts with its water when heated. It dissolves in acids, forming solutions which are dark brown when concentrated, reddish-yellow when dilute.

The *trioxide*, or *Periridic oxide*, Ir^2O^3 or $IrrO^3$ is formed, according to Claus, when iridium is fused for some time with nitre. The resulting blackish-green mass dissolves in water, forming a deep indigo-coloured solution of basic periridiate of potassium, leaving a black crystalline powder consisting of acid periridiate. This powder, when washed, is perfectly neutral and tasteless, and dissolves with indigo-colour in hydrochloric acid, giving off a very large quantity of chlorine. The quantity of potash in it is variable, but the iridium and oxygen (in the acid) constantly maintain the proportion of 1 to 3. (Claus, Ann. Ch. Pharm. lix. 249.)

IRIDIUM, OXYGEN-SALTS OF. Iridium, like the other platinum-metals, shows but little tendency to form oxygen-salts. The oxides dissolve in acids, but no definite salts are obtained in this way. The solution of iridic oxide in sulphuric acid has a dark brown colour, which is not modified by potash in the same manner as that of the dichloride, neither does it yield any blue precipitate on boiling.

The only definite oxygen-salts of iridium that have been obtained are double salts, containing sulphurous and hyposulphuric acids.

a. Hypo-iridoso-potassic Sulphite. $3(K^2O.SO^2).Ir^2O.2SO^2 = \left.\begin{matrix}(\overset{\prime\prime}{SO})^4\\ Ir^2K^6\end{matrix}\right\}O^8.SO^2$.—This salt is obtained as a white powder when the mother-liquor obtained in preparing chloriridite of potassium by passing sulphurous anhydride through a solution of the chloriridiate (p. 318), is evaporated to a small bulk. It is somewhat crystalline, nearly tasteless, insoluble in water, but dissolves easily in hydrochloric acid, giving off sulphurous anhydride, and yielding a yellow prismatic salt, in which 3 at. SO^2 are replaced by 6 at. Cl. It dissolves in potash, forming a solution which is decomposed by heat, with separation of blue iridic hydrate. The crystals contain 5 at. water, which is given off at 180° ; at a higher temperature, the salt is completely decomposed. (Claus, Ann. Ch. Pharm. lxiii. 352.)

β. Acid Hypo-iridious Sulphite with Chloride of Potassium, $6KCl.(Ir^2O.2SO^2)$.—Produced by treating the salt *α* with hydrochloric acid. The resulting yellow solution yields by evaporation, pale yellow prisms, very soluble in water, and having an astringent somewhat sweetish taste. At a red-heat it gives off sulphurous anhydride, and leaves a mixture of metallic iridium with chloride and sulphate of potassium. (Claus, *loc. cit.*)

γ. A salt containing $2(2KCl.IrCl).(2K^2SO^3.Ir^2SO^3.SO^2).12H^2O$ is obtained by heating a solution of chloriridite of potassium with acid sulphite of potassium till the green colour changes to red, and carefully evaporating. It forms minium-red crystals, yields protoxide of iridium when treated with carbonate of potassium in an atmosphere of carbonic anhydride, and is converted by prolonged heating with acid sulphite of potassium, into the white salt, *α*. (Claus, Ann. Ch. Pharm. cvii. 129). In a former memoir (Ann. Ch. Pharm. lxiii. 344–348) Claus represented this salt by the formula $2(KO.SO^2).\ 2KCl.\ 2IrO.S^2O^4Cl$, in which the protoxide of iridium was supposed to be combined with a chloro-hyposulphuric anhydride S^2O^4Cl. The same acid may be supposed to exist in the two following salts:

δ. $4KCl.2IrO.S^2O^4Cl$.—Formed by treating the preceding salt with hydrochloric acid. Deep red prismatic crystals, easily soluble, with yellow colour, in water, insoluble in alcohol. The air-dried crystals contain 5 and 6 per cent. water ($= 4HO$), which is given off at 180°. Alkalis slowly decompose the salt, and nitromuriatic acid converts it, after some time, into an iridic salt. Its composition might also be represented by the formula $2KSO^3.(2KCl.Ir^2Cl^3)$; but it appears to contain a proto- rather than a sesqui-compound of iridium.

ε. $4(KO.SO^2).IrO.S^2O^4Cl$.—This salt is contained in the mother-liquor of *δ*, and separates as a translucent, amber-coloured, viscid mass, which dries up to an amorphous translucent substance, yielding a yellow powder. It is decomposed by water, part of it dissolving, while the rest is converted into the white salt *α*. (Claus, Ann. Ch. Pharm. lxiii. 351; see also *Gmelin's Hand-book*, vi. 388.)

IRIDIUM, SULPHIDES OF. Four of these compounds are described, analogous to the oxides, and obtained by precipitating the solutions of the chlorides with sulphydric acid. The *protosulphide*, Ir^2S, obtained also by heating either of the higher sulphides in a close vessel, is grey or blackish-blue. According to Berzelius, it dissolves in nitric acid, forming hypo-iridious or iridious sulphate; and in sulphide of potassium more easily than sulphide of platinum. The *sesquisulphide*, Ir^4S^3, is a brown-black precipitate, sparingly soluble in water [? when partially oxidised], and behaving like the protosulphide with nitric acid and sulphide of potassium (Berzelius). The *disulphide*, Ir^2S^2, is obtained by precipitation, also by igniting chloriridiate of ammonium with an equal weight of sulphur (Vauquelin); by igniting pulverulent iridium with sulphur and an alkaline carbonate, and exhausting the product with water (Fellenberg, Pogg. Ann. lix. 66); and by mixing a solution of dichloride of iridium in strong alcohol with sulphide of carbon, and leaving the mixture in a closed vessel for a week. It is then converted into a gelatinous mass, which is to be broken up, collected on a filter, washed with alcohol, then repeatedly boiled with water, filtered and dried. The product thus obtained is disulphide of iridium. It is a dark yellow-brown powder, which is decomposed by heat, leaving the protosulphide or metallic iridium according to the temperature to which it is raised. The disulphide obtained by precipitation behaves with nitric acid and with sulphide of potassium like the protosulphide. The *trisulphide*, Ir^2S^3, is obtained by decomposing the trichloride with sulphydric acid, but to complete the decomposition, the liquid saturated with sulphydric acid must be left for a considerable time in a closed vessel at 60°. It is a dark yellow-brown precipitate, which behaves like the preceding compounds with nitric acid and sulphide of potassium. (Berzelius.)

IRIDIUM-BASES, AMMONIACAL. *Ammonio-protochloride of iridium*, $NH^3.IrCl$, or *Chloride of iridammonium*, $NH^3Ir.Cl$, is prepared by heating dichloride of iridium till it is converted into proto-chloride, dissolving the brown resinous residue in carbonate of ammonia, and adding hydrochloric acid in slight excess. The compound then separates in the form of a yellow granular precipitate, insoluble in water. The oxide corresponding to this chloride has not been obtained in the free state. The *sulphate*, $(NH^3Ir)^2,SO^4$, is obtained by heating the chloride with dilute sulphuric acid. It crystallises in large orange-yellow laminæ, easily soluble in water.—*Diammonio-protochloride of iridium*, $2NH^3.IrCl$, or *Chloride of ammiridammonium*, $\overbrace{NH^2(NH^4)}Ir.Cl$, is obtained as a white precipitate, by boiling the compound, $NH^3Ir.Cl$, with excess of ammonia. Treated with moderately strong sulphuric acid, it yields the corresponding sulphate $(\overbrace{NH^2(NH^4)Ir})^2SO^4$, in rhombic prisms; and, by decomposing this salt with nitrate of barium, or the chloride with nitric acid, the nitrate is obtained in yellow needles, which dissolve readily in water, melt when heated, and then suddenly decompose with flame.—*Chloronitrate of ammiridammonium*, $\overbrace{NH^2(NH^4)Ir}\left\{\begin{matrix}NO^3\\Cl\end{matrix}\right.$, or *Nitrate of ammochloriridammonium*, $\overbrace{NH^2(NH^4)}(IrCl).NO^3$, analogous to Gros' platinum-nitrate, is obtained as a yellowish, crystalline, granular mass, by heating the chloride of iridammonium, NH^3IrCl, with strong nitric acid; when recrystallised from water, it forms shining, yellow, laminar crystals.—*Dichloride of ammiridammonium*, $NH^2(NH^4)Ir.Cl^2$, or *Chloride of ammochloriridammonium*, $\overbrace{NH^2(NH^4)IrCl}).Cl$, is obtained by treating the last-mentioned salt with hydrochloric acid, in the form of a violet precipitate, which dissolves readily in hot water, and separates from the solution in violet crystals. Nitrate of silver added to the solution throws down only half the chlorine. The nitrate, treated with dilute sulphuric acid, yields the chlorosulphate of ammiridammonium, in delicate greenish, needle-shaped crystals. (Skoblikoff, Ann. Ch. Pharm. lxxxiv. 275.)

The compound $5NH^3.Ir^2Cl^3$, or $\left.\begin{matrix}\overbrace{NH^2(NH^4)Ir}\\\overbrace{NH(NH^4)^2Ir}\end{matrix}\right\}Cl^3$, is obtained by mixing a dilute solution of chloriridite of ammonium, $(NH^4)^3Ir^2Cl^6$, with excess of ammonia, and leaving the mixture in a well-closed and completely filled bottle for some weeks in a warm place; heating the liquid, which has then acquired a rose colour, to expel the excess of ammonia; neutralising with hydrochloric acid, evaporating to dryness, and treating the greenish-yellow residue with cold water to extract the chloride of ammonium. A light flesh-coloured, finely crystalline powder then remains, which, when dissolved in boiling water acidulated with hydrochloric acid, yields on cooling, a crystalline precipitate of $5NH^3.Ir^2Cl^3$, mixed with sesquichloride of iridium. This compound, when dissolved in a boiling solution of ammonia, is partially decomposed, with separation of blue hydrated dioxide of iridium; when digested with water and oxide of silver, it yields a rose-coloured alkaline solution of the base $10NH^3.Ir^4O^3$. This solution, saturated with various acids, yields crystalline salts, soluble in water, namely, a *carbonate*, $10NH^3.Ir^4O^3.3HCO^3$, as a light flesh-coloured, finely crystalline, alkaline powder; a *nitrate*, $10NH^3.Ir^4O^3.3NO^5$, in indistinct, light flesh-coloured, neutral prisms; and a sulphate, $10NH^3.Ir^4O^3.3SO^3$, also neutral and of similar colour. (Claus, *Beiträge zur Geschichte der Platin-metalle*, Dorpat, 1854; Jahresb. 1854, p. 434.)

IRIDOSMINE. *Native iridium, Osmide of Iridium, Osmium-iridium, Iridosmium, Newjanskite, Sisserskite.*—This compound occurs, together with platinum, in the province of Choco in South America, in California, Oregon, Australia, and in the Ural mountains; also in the gold washings on the rivers du Loup and des Plates, Canada. It sometimes constitutes the principal part of platinum ore, especially of that from Katharinenberg, Slatoust, and Kiseltin in the Ural. It occurs rarely in hexagonal prisms with replaced basal edges, commonly in irregular grains, flat or round, sometimes in very thin laminæ. It has a metallic lustre, tin-white or light steel-grey colour, and is slightly malleable. Hardness = 6 to 7. Specific gravity = 19·3 to 21·12.

The following are analyses of specimens from different localities:—1. By Thomson (*Gmelin's Handbook*, vi. 425).—2. By Claus (*Beiträge &c.*).—3. By Berzelius (Pogg. Ann. xxxii. 232).—4–8. Deville and Debray (Ann. Ch. Phys. [3] lvi. 385; Jahresb. 1859, p. 767).

	Os.	Ir.	Rh.	Pt.	Ru.	Cu.	Fe.	
1. Brazil	21·50	72·90	. .	. .	. .	. .	2·60	= 100
2. Nischna Tagilsk, *hexagonal plates*	27·32	51·24	1·51	10·08	5·85	. .	. . .	= 100
3. Katharinenberg, *laminæ*	49·34	46·77	3·45	. .	. .	. .	0·74	= 100
4. Oregon, *thin shining scales*	17·20	70·40	12·30	0·10	6·00	. .	. .	= 100
5. ,, *round compact grains*	35·10	57·80	0·63	. .	6·37	0·06	0·10	= 100
6. California, *Cavernous nodules*, sometimes filled with oxide of iron or chromic iron ore	43·40	53·50	2·60	. .	0·50	. .	. .	= 100
7. Australia, *extremely thin laminæ*	33·46	58·13	3·04	. .	5·22	0·15	. .	= 100
8. Borneo	38·94	58·27	2·64	0·15	. .	. .	. .	= 100

Iridosmine has usually been regarded as consisting of definite osmides of iridium (the iridium being more or less replaced by rhodium, ruthenium, and platinum); No. 1 agreeing nearly with the formula Ir^3Os; 2, with $IrOs$; and 3, with $IrOs^3$. But according to Deville and Debray, it is not a homogeneous substance, and cannot be regarded as a distinct mineral species.

Iridosmine, when heated in the air, gives off osmic acid, with greater facility as it is richer in osmium, and becomes dull. When ignited for some time with nitre alone, or with nitre and caustic potash, it gives off part of the osmium as osmic acid, and forms osmate of potassium, together with iridiate of potassium (p. 314). According to Fischer (Pogg. Ann. xviii. 258) it is more easily decomposed by nitrate of calcium, and according to Deville and Debray (p. 316) by a mixture of peroxide and nitrate of barium. Nitromuriatic acid has scarcely any action upon it. [For the methods of analysing it, see IRIDIUM, pp. 315, 316, 320; also PLATINUM-RESIDUES.]

IRISINE. See CHINOLINE (i. 871).

IRITE. This name was given by Hermann, J. pr. Chem. xxiii. 276) to a black mineral from the Ural, crystallised in regular octahedrons and consisting of the protoxides of iridium, osmium, and iron, combined with the sesquioxides of iron and chromium. According to Claus (*ibid.* lxxx. 285) it is a very variable mixture, consisting chiefly of iridosmine and chrome-iron ore.

IRON. Synonyms: *Eisen; Fer; Ferrum; Mars.* Symbols and atomic weights: Fe = 28; Ffe = 56. Equivalents: Fe = 28 (ferrosum); fe = 18⅔ (ferricum).

This metal, although the most abundant of the heavy metals, and most largely employed in the arts, is but little known in a state of absolute chemical purity. The iron met with in commerce always contains carbon, and generally some other foreign substances, altogether varying in amount from 0·5 to nearly 10 per cent. Probably all these admixtures exercise some influence on the characters of the metal; but it appears to be chiefly the amount of carbon contained in iron, which determines the remarkable differences of character presented by the several varieties of metallic iron known as malleable iron, cast iron, and steel.

Pure iron is described as resembling silver in whiteness, capable of receiving a very high polish, extremely tenacious, softer than ordinary malleable iron, and presenting a scaly, conchoïdal, or sometimes crystalline fracture. Specific gravity, after melting 7·8439, in sheet or wire 7·75 to 7·60.

Iron obtained by electrolysis was found to have a specific gravity of 8·1393. Its malleability was not affected by heating to redness and rapid cooling, nor was it in the least degree hardened by this treatment. It was scarcely acted upon by acids at the ordinary temperature; but dissolved with the aid of heat, evolving hydrogen quite free from the peculiar smell observable in the hydrogen evolved during the solution of ordinary iron. (Percy, *Metallurgy*, ii. 2.)

The crystalline form of iron is either the cube, octahedron, or some other form belonging to the regular system.

The different kinds of iron employed in the arts may be comprised under three heads, viz. malleable iron, cast iron, and steel, the latter being to some extent intermediate in its characters between the other two, and combining some of the peculiarities of both. See STEEL.

The difference between these three kinds of iron is, however, by no means absolute, even as regards their characters, but more a difference in the degree in which particular characters are presented. Iron approaching nearest to a state of purity requires a very high temperature for its fusion, while cast iron melts at a comparatively low heat, but, not being sufficiently malleable, it cannot be wrought into any required shape. Malleable iron has a much higher degree of toughness or tenacity than cast iron, which on the other hand is much harder, while steel may be melted and forged, as well as rendered hard or soft at will, or as it is technically termed "tempered," by cooling suddenly or gradually; on account of these varied combinations of qualities, the different kinds of iron have a wide range of applicability to a great diversity of purposes.

Leaving out of consideration for the present all the other substances met with in iron except carbon, it appears that the greater or less approximation to the character of pure iron is so uniformly accompanied by very slight differences in the amount of carbon, that these two circumstances may be regarded as having a very intimate causal connection.

Karsten's observations lead to the conclusion that iron containing 0·65 per cent. carbon, and free from any other substance, becomes so much hardened by plunging it into water, while red-hot, that it may be regarded as steel. When the amount of carbon is as much as 1·4 or 1·5 per cent. the metal presents the maximum combination of tenacity with the capability of hardening by sudden cooling. Increase in the amount of carbon beyond this limit is accompanied by increased hardness, but the tenacity and malleability are less. With 1·75 per cent. carbon, the malleability of the metal is very slight, and with 1·9 per cent. it scarcely admits of being wrought. Iron with 2·3 per cent. carbon presents, when melted and gradually cooled, indications of graphite being separated during the cooling, and the other characters of cast iron, which may contain an amount of carbon varying from this minimum limit up to 5·75 per cent.

These limits, however, are somewhat different when iron contains other substances, as is usually the case: thus, taking as the criterion between malleable iron and steel, the capability of acquiring, by sudden cooling, such a degree of hardness as to give sparks when struck with flint, this is generally found to obtain with iron containing 0·5 per cent. when it also contains small quantities of silicon, sulphur, phosphorus, &c.

Taking as the criterion which distinguishes cast iron from steel, the separation of graphite when the melted metal is slowly cooled, and the want of malleability in the cold, it is found, in like manner, that the relation between these characters and the amount of carbon is not strictly constant, but that it is to some extent modified by the nature and amount of other admixtures, not only by their rendering the metal less malleable, but also by their promoting the tendency to the separation of carbon.

Malleable Iron (*Schmiedeisen; Stabeisen; Fer doux*).—Ordinary malleable iron has a grey colour, which varies in its shade according to the character of the iron, and has sometimes a bluish or blackish tinge.

The specific gravity varies between 7·3 and 7·9; that of the better kinds generally approximating to the mean of these two values. The specific gravity is affected to some extent by the alteration of internal texture produced mechanically. Thus a bar 4 inches wide and 1 inch thick with a specific gravity = 7·8010 acquired a specific gravity = 7·8621 when rolled out to very thin sheet, and iron of specific gravity 7·7938 acquired a specific gravity = 7·8425 when drawn into very thin wire. (Karsten.)

The specific heat of ordinary malleable iron is 0 113795, and is somewhat higher when the amount of carbon in the metal is large. (Regnault.)

The conducting power for heat is 374·3 compared with gold = 1000. (Despretz.)

The linear and cubical expansion by heat (see HEAT, iii. 68, 71) is less than that of most other metals. The linear expansion for each degree between 100° and 300° C. $= \frac{1}{88100}$. (Dulong and Petit.)

An iron bar expands $\frac{3}{560}$ when raised from a red heat to a white heat, and $\frac{1}{560}$ when heated from 20° C. to whiteness. (Rinman.)

The melting point of malleable iron has not been determined with any degree of certainty. It is between the melting point of cast iron and that of platinum, and is estimated at 1550° C. by Pouillet, and at 2000° C. by Scheerer, and there is no doubt that it is higher in proportion as the metal contains less carbon.

Pure iron is attracted by the magnet more powerfully than iron containing carbon, and it may be rendered magnetic; but it does not retain the magnetic condition so long as iron containing some carbon. Ordinary bar iron is also attracted more strongly than steel, and is more easily rendered magnetic, but loses the polar condition much sooner than steel does. It appears therefore that the presence of a certain amount of carbon is in some way necessary for the retention of the magnetic condition by iron. Bars of iron placed vertically or nearly so become, in course of time, magnetic. The magnetic condition of iron is very nearly destroyed by a red heat, and entirely so by exposure to a white heat.

The electric conductivity of iron is much less than that of copper. Taking this as = 100, that of iron is = 20 (Harris), 15·8 (Becquerel), 17·74 (Lenz). Matthiessen considers that the electric conductivity of electro-deposited iron is much higher than that of ordinary malleable iron.

	Conductivity at 0° C.	Percentage decrement in conductivity between 0° and 100° C.	Deduced conductivity of pure iron. at 0° C.
Electrotype iron	100	38·3	
Plate iron . .	91·8	36·0	102·7
	72·8	34·1	102·1
	84·6	34·7	99·2

The hardness of malleable iron varies considerably; it is influenced by the presence of foreign substances, and reduced by increase of temperature. It is however but very slightly increased by sudden cooling of the red-hot metal; the less so the smaller the amount of carbon contained in it. A certain amount of carbon seems essential to the hardness of malleable iron. Absolutely pure iron is so soft that it offers but little resistance to friction.

The tenacity of iron also varies widely, and is influenced by the nature and amount of foreign admixture in the metal, as well as by its internal texture, by temperature, and by other conditions. Up to a temperature of 146° C., the tenacity of boiler plate is not sensibly diminished; but at a red heat it is reduced one fourth. The tenacity of good rivet iron at 190° C. is a third greater than at the ordinary temperature; but at a red heat it is reduced to nearly one half. (Fairbairn, *Useful Information for Engineers.*)

Tenacity or tensile strength of iron.

Kind of iron.	Lengthwise in pounds per square inch.	Crosswise in pounds per square inch.	Ultimate extension.	Authority.
Lowmoor iron wire	64,200	52,490	. .	Fairbairn.
Staffordshire bar iron	from 62,231 to 56,715	. .	0·302 0·186	Kirkaldy and Napier.
Swedish bar iron	from 48,232 to 47,855	. .	0·264 0·278	,,

(See Kirkaldy, Trans. Instit. of Engineers in Scotland, 1858–9; and *Tensile Strength of Wrought Iron and Steel*, London, 1862.—Fairbairn, Brit. Assoc. Report, 1856.)

The malleability of iron is very considerable, though less than that of silver or gold. It is influenced by the presence of foreign substances which modify the hardness and tenacity, the degree of malleability being apparently determined by the relative hardness and tenacity, and to some extent also by its internal texture. The malleability of iron is increased in proportion as its temperature is raised, inasmuch as it then becomes softer without its tenacity being proportionally lessened. At a red heat it is sufficiently soft to be brought to any required shape by hammering or rolling, and at a white heat it becomes quite pasty, so that separate pieces may be, as it were, kneaded together into one mass; or, as it is termed, *welded*. This capability of being forged and welded, so important as regards the methods by which iron is wrought for various uses, is referable to the wide interval between the temperature at which the metal presents its ordinary degree of hardness, and that at which it becomes liquid; as well as to the fact that, at temperatures far below the melting point, it acquires a soft plastic condition, which is retained in a greater or less degree through a considerable range of temperature.

Among the foreign substances influencing prejudicially the malleability of iron, the chief are sulphur, phosphorus, and silicon. The first communicates to it the character of being brittle while hot, or, as it is called, "red short" in forging. Phosphorus renders iron "cold short," or brittle and weak at the ordinary temperature. Silicon has a similar influence in a higher degree. Manganese seems to be beneficial rather than otherwise as regards the malleability of iron. The malleability of iron is considerably reduced by immersing it while red-hot in cold water, as well as by long continued hammering and by rolling, but it is again restored by heating the metal to redness, and allowing it to cool gradually.

The texture, or molecular structure of iron varies very considerably according to the treatment to which it has been subjected. After being melted, iron is decidedly crystalline or granular, and its fracture presents distinct indications of that condition. By hammering or rolling while hot, it acquires a fibrous or silky texture, becomes more tenacious, less susceptible of true fracture, and capable only of being torn asunder. In the usual method of producing malleable iron, it is not melted, but wrought mechanically while in a kind of doughy condition, and the uniform close fibrous texture which determines the quality of the metal depends much upon the nature of this treatment and the extent to which it is carried.

By hammering while cold, fibrous iron is rendered harder and brittle; when afterwards broken, it presents a granular or crystalline fracture, but opinions differ as to whether this crystalline condition be really a result of the hammering. This is also the case with regard to the influence of long continued pressure, vibration, or concussive action, in affecting the texture of iron, some maintaining that these conditions slowly destroy the fibrous texture, rendering the iron crystalline and thereby weaker. (Rankine, Proceedings of Inst. of Civil Engineers, 1843; Percy, *Metallurgy*, ii. 8.)

Malleable iron undergoes no change in dry air, or in water free from air; but in moist air, or in water containing air, it gradually becomes oxidised or rusted, from the surface inwards, until eventually the entire mass may be converted into oxide. The carbonic acid present in atmospheric air appears to contribute largely to the production of this change. The presence of saline substances in water also facilitates the oxidation of iron; while alkalis, and oily or resinous substances, retard the oxidation. (Mallet, *Action of air and water, &c., upon cast iron, wrought iron, and steel*, Brit. Assoc. Reports, 1838, p. 253; 1840, p. 221.) Contact with more highly electro-positive metals, such as zinc, also hinders the oxidation of iron within a certain distance around the point of contact.

At a temperature about 230° C., iron becomes capable of combining directly with atmospheric oxygen, and the polished surface at first becomes covered with an extremely thin film of magnetic oxide, of a yellow colour which gradually passes into red, blue, and grey. At a red heat this crust of oxide—*forge scale*—becomes thicker, and gradually passes at its outer surface into ferric oxide. At a white heat, iron burns in the air, with production of magnetic oxide, and this combustion may be sustained for some time by directing a blast of air upon the metal.

At a temperature about 360° C. iron decomposes water-vapour, forming magnetic oxide and liberating hydrogen.

Pure iron dissolves completely in moderately dilute acids. Ordinary malleable iron dissolves completely in strong hydrochloric acid: but with dilute acid a carbonaceous residue remains undissolved. In both cases also the hydrogen evolved carries with it carbonaceous vapour, which communicates to it a peculiar smell.

Malleable iron generally contains from 0·25 to 0·5 per cent. carbon; sometimes the amount is much less. The smaller the amount of carbon, the softer is the iron, and

Analyses of best qualities of Foreign Malleable Iron.

Source	Swedish.				Silesian;	Russian iron.		Swedish.	Mägdesprung.		Dannemora.
	Österby.	Gysinge.	Löfsta.		Rybnik.			Kloster.			
	o o	Ⓑ	Ⓛ			ECND	K.ЗKE	➤K→			
Analyst	Henry.			Karsten.		Henry.			Bromeis.		Schafhäutl.
Iron	99·863	99·720	99·544	99·73	99·873	99·412	99·594	98 605	98·88	99·13	98·78
Carbon	0·054	0·087	0 087	0·24	0·090	0·272	0·340	0·356	0·40	0·66	0 84
Silicon	0·028	0·056	0·115	0·03	0 030	0·062	trace	0·252	0·01	trace	0·12
* Sulphur	* 0·055	* 0·132	* 0·220	. .	0·007	* 0·234	* 0·066	* 0·787	trace		
Phosphorus	trace	0·005	0·034	trace	. .	. .	. .	trace	. .		. .
Manganese	trace	. .	. .	trace	. .	0·020	trace	trace	0·30	0·29	0·05
Copper	. .	. .	. .	. .	. .	.	. .	. .	0·32	0·05	0·07
Arsenic	. .	trace	trace	. .	. .	trace	. .	. .	. .	. .	0 02
	100·000	100·000	100·000	100·000	100·000	100·000	100·000	100·000	99·91	100·13	99·88

Analyses of British Malleable Iron.

	South Wales.				Shropshire.
		Puddled bar.			Best bar.
Works		Dowlais.			
Analyst	Schafhäutl.	Riley.		Price.	
Iron	98·90	7·72	98·54		
Carbon	0·41	.		not estimated	
Silicon	0·08	0·26	0·13	0·18	0·18
Sulphur	. .	0·21	0·05	0·06	0·03
Phosphorus	0·40	0·71	0·42	0·37	0·30
Manganese	0·04				
Manganese, nickel and cobalt	. .	0·03	0·22	. .	trace
	99·83	100·00	100·00		

Armour and Boiler Plate.

Works	Lowmoor	Thames Iron Coy.	Beale & Co.	Shortridge & Howell.		Weardale.	Russell's Hall.
Analyst	Tookey.	Percy.	Percy.	Percy.	Percy. La Gloire.	Percy.	Henry.
Iron	99·372	. .	. .	. .	. .	. .	99·361
Carbon	0·016	0·033	0·044	0·230	0·143	0·170	0·190
Silicon	0·122	0·160	0·174	0·014	. .	0·110	0·144
* Sulphur	*0·104	*0·121	*0·118	*0·190	*0·058	*0·058	*0·165
Phosphorus	0·106	0·173	0·228	0·020	0·030	0·089	0·140
Manganese	0·280	0·029	0·250	0·110	. .	0·330	. .
Nickel	trace						
Cobalt	trace	trace	trace	trace	. .	trace	. .
	100·000						100·000
Specific gravity	7·8083	7·7035	7·6322	7·9042	. .	. .	. .
Tensile strength	24·644	23·354	24·171	27·032	. .	. .	. .
Relative resistance to punching	1000	907	873	1168	. .	. .	. .

* The results to which this mark * is put are probably much too high. See *Estimation of Sulphur*, p. 372.

the larger the amount, the nearer does it approximate to the character of steel. The only iron that is probably quite free from carbon is that known technically as "burnt iron," which cannot be soundly welded. Hence it has been supposed that the capability of being welded is determined by the presence of carbon in iron. There are, however, no good reasons for this opinion; it is more probable that the peculiarity of "burnt iron" is only indirectly due to the absence of carbon, and is determined by the presence, in the metal, of a minute quantity of oxide, which could not have been introduced so long as it still retained any carbon.

Among the foreign substances, other than carbon, present in malleable iron, the most important are sulphur, phosphorus, and silicon, existing probably in combination with equivalent proportions of the metal, as sulphide, phosphide, and silicide.

Sulphur is generally present to some extent in malleable iron, and, even when amounting to only 0·034 per cent., has the effect of rendering it "red short," and liable to crack at the edges in forging. It has been considered that 0·01 per cent. is the highest amount consistent with the usefulness of the iron. (Karsten, *Handbuch der Eisenhüttenkunde*, 423.)

Phosphorus is also frequently present, and, when amounting to 0·75 per cent., renders the iron very weak and brittle at the ordinary temperature, or, as it is called, "cold short." In smaller amount, it is considered to be serviceable in rendering the iron more capable of being welded. (Karsten, *op. cit.*)

Silicon renders iron harder and lessens its tenacity, making it what is termed "rotten" in working, even when present to the extent of only 0·37 per cent.

Manganese is considered to render iron harder, but not to make it steely.

Copper is considered to render iron "red short," and to reduce the capability of being welded, without however affecting the tenacity of the metal.

It may, however, be safely said that the evidence upon which the above opinions, as to the influence of these admixtures upon the character of malleable iron, are founded, is much too slender, and it is very desirable that this subject should be more thoroughly investigated.

The characters of *steel*, and the methods of manufacturing it, will be treated of in a separate article.

Cast Iron, Pig Iron (*Roheisen; Gusseisen; Fonte*).—There are two essentially distinct kinds of cast iron, viz. grey and white.

Grey cast iron (*Graues Roheisen; Fonte grise*) varies in colour from pale to dark grey. It has generally some slight degree of malleability; but is harder and more brittle than malleable iron. Its texture is granular; sometimes very fine-grained, sometimes coarse-grained at the fracture, with minute particles of graphite visible throughout the mass.

White cast iron (*Weisses Roheisen, Fonte blanche*) varies in colour from that of tin to pale grey. It is very hard and brittle; of crystalline lamellar texture, and sometimes vesicular. The fracture is shining, and varies from lamellar to compact and conchoïdal, in proportion as the colour varies from tin-white to grey. The most characteristic variety is called *specular iron* (*Spiegeleisen; fontes lamelleuses*).

The specific gravity of grey cast iron is, on the average, 7·1; that of white cast iron is, on the average, 7·5.

Grey cast iron melts at about 1600° C., and more easily in proportion as the amount of carbon it contains is greater. White cast iron melts at a lower temperature; but it does not become so liquid when melted as the grey cast iron, which passes suddenly from the solid to the liquid state, while the white cast iron remains in a pasty state for some time. Melted cast iron dissolves malleable iron, and is thus rendered tougher and stronger than originally (toughened cast iron). White iron, when cooled very gradually from the melted state, is converted into grey cast iron. Grey cast iron, on the contrary, when very gradually cooled from a melted state, is not altered except in becoming softer and more malleable; but when rapidly cooled, it is converted into white cast iron, more or less completely in proportion as the amount of carbon it contains is greater or less. On this account the outer surface of a casting has a hard crust or "skin," as it is called, in consequence of the more rapid cooling of that portion of the melted metal which comes in contact with the sides of the mould, and its conversion into white cast iron. This effect is often augmented, in practice, by lining the mould with iron plates, so as to facilitate the rapid cooling of the outer portions of the casting, and produce a layer of white cast iron, from ⅛ to ¼ an inch thick, while the interior retains the condition of grey cast iron, thus combining the particular advantages of white cast iron as regards hardness, and of grey cast iron as regards strength.

It has been observed that in large masses of cast iron there is an inequality in the amount of carbon contained in the metal at the exterior and interior portions. In masses which have been gradually cooled from a melted state, the centre portion contains less carbon than the exterior portions. There is also a further difference as to the condition in which the carbon exists. At the centre, the relative proportion of graphitic carbon as compared with combined carbon, is greater than it is at the exterior portions. This latter difference will be more marked in proportion as the melted metal is more rapidly solidified at the surface. In one instance of iron cast in an iron mould, referred to by Karsten, the following results were obtained:—

	Total quantity of carbon.	Combined carbon.	Graphite.
Cast iron before melting . . .	4·0281 . .	= 0·7812 . .	3·2469
Outer white portion of casting . .	5·0929 . .	= 5·0929	
Inner grey portion of casting . .	3·8047 . .	= 0·6106 . .	3·1941

The main chemical difference between white and grey cast iron consists in the state in which the carbon they contain exists. In specular iron, the whole of the carbon is combined with iron, while in the most characteristic kind of grey cast iron, when solid, at least, the greater part of the carbon is merely mixed with the iron, in the state of graphite, and only a portion of it is in a state of combination. Between these two extremes there are a variety of intermediate states in which white and grey cast iron are mixed together in various proportions, constituting what is known as *mottled cast iron* (*halbirtes Gusseisen ; fonte truitée*).

The hardness and strength of these varieties of cast iron differ considerably; as a rule, the grey is stronger than the white, and this again is harder than the grey. White cast iron is, however, too brittle to be used for structures, except for the purpose of coating the surface of castings with a hard crust or skin, by casting in moulds lined with metal (chill casting). (Rankine, *Civil Engineering*, p. 499.)

The tenacity of cast iron is very much less than that of malleable iron; but its capability of resisting crushing force is very much greater.

Kind of iron.	Direct Tenacity.	Resistance to direct crushing.	Modulus of rupture of square bars.	Modulus of Elasticity.
	In pounds per square inch.			
Cold blast . .	from 12,694	56,455	36,693	14,000,000
	to 18,855	102,408	39,609	17,036,000
Hot blast . .	from 13,434	72,193	29,889	11,639,000
	to 23,468	104,881	43,497	22,733,000
Toughened cast iron	from 23,461	129,876		
	to 25,764	119,457		

The strength of cast iron is increased by remelting, but reduced when the melting is repeated several times. At very low temperatures it becomes more brittle and weaker. (Fairbairn and Hodgkinson, *Report on the Application of Iron to Railway Structures*, p. 265.)

The specific heat of specular iron = 0·12983, that of ordinary white cast iron = 0·12728. (Regnault.)

The linear expansion of cast iron by heat is greater than that of malleable iron, amounting to $\frac{7}{560}$ between 20° and 560° C. (red heat), and $\frac{12}{560}$ between 20° and a white heat. (Rinman.)

Pieces of cold cast iron thrown into the melted metal sink to the bottom; but when they have a temperature near the melting point, they float on the surface of the melted metal. Hence it would appear that some degree of contraction takes place in the passage from the solid to the liquid state. This character of cast iron is important as regards its application to casting: for the increment of bulk attending solidification ensures the perfect filling of the moulds at that moment, and the production of sharp, well-defined castings. But the greatest amount of expansion or contraction takes place just below the melting point. On account of this contraction between a temperature near the melting point and the ordinary atmospheric temperature, it is necessary to make the moulds for castings proportionately larger than the castings are required to be. The contraction of grey cast iron amounts to about 1 per cent.; that of white cast iron is from 2 to 2·5 per cent. of the linear dimensions. The allowance generally made for this "shrinkage" in casting is $\frac{1}{96}$ or one eighth of an inch in a foot. Cast iron also undergoes a permanent increase of bulk under the long-continued influence of heat. (Percy, *Metallurgy*, ii. 872.)

White cast iron exposed to oxidising influences at the ordinary temperature, rusts much more slowly than grey cast iron, and this again, provided it does not contain much sulphur or other readily oxidisable substances, more slowly than malleable iron. Specular iron is but very little liable to oxidation.

At an elevated temperature, grey cast iron becomes coloured by oxidation sooner than malleable iron; white cast iron on the contrary becomes coloured even sooner than steel. When cast iron is heated to redness in the air, the carbon it contains is first oxidised and the metal rendered more or less malleable; then a crust of magnetic oxide is formed at the surface and gradually increases in thickness as in the case of malleable iron. Grey cast iron is most slowly oxidised in this way, and becomes porous and friable after abstraction of its carbon. White cast iron is decarbonised more rapidly, and acquires a malleable steely character. Upon this fact is based the manufacture of malleable cast iron, which consists in heating to redness the castings, while imbedded in powdered chalk, charcoal, or oxide of iron, so as to be partially protected from the oxidising influence of the air.

Cast iron melted in contact with air becomes covered with a crust of oxide, and by removing this crust from time to time, it may be entirely converted into oxide. If the crust is allowed to remain in contact with the melted metal, this gradually becomes decarbonised, steely and less fusible. White cast iron heated in contact with air till it assumes the pasty condition, is decarbonised much more rapidly than by mere heating to redness, and passes from the steely condition to that of pure iron, without so great a degree of oxidation as takes place when the metal is melted. The most important method of manufacturing malleable iron is based upon this fact (puddling).

Cast iron melted under soda, potash, lime, or magnesia carbonates, is gradually decarbonised, and may be wholly converted into malleable iron, if the heat be raised as the iron becomes less fusible.

Atmospheric air forced into melted cast iron oxidises the carbon and silicon, as well as part of the iron, and converts the remainder into malleable iron. The temperature produced in this way is sufficiently high to determine the fusion of the wholly decarbonised iron. (See STEEL.)

White cast iron heated with concentrated hydrochloric acid is entirely dissolved; but grey cast iron, treated in the same way, leaves a residuum of graphite. In both cases the combined carbon enters into combination with a portion of the nascent hydrogen eliminated by the solution of the iron, forming volatile oily hydrocarbons, the vapour of which communicates a peculiar smell to the gas evolved. This oily substance, which appears to be of a nature analogous to petroleum, also collects as a thin film on the surface of the acid solution.

The action of dilute hydrochloric acid upon cast iron is somewhat different. Specular iron is acted upon very slowly at the ordinary temperature, but with the aid of heat, both it and grey cast iron are readily dissolved. The hydrogen evolved has the characteristic smell, but the amount of the hydrocarbons formed appears to be smaller than when concentrated acid is employed. White cast iron leaves a bulky dark-brown carbonaceous residue, which is soluble in potash, and, when washed and dried is very readily combustible, leaving a black residue containing silica (Daniell, Journal of Science and the Arts, ii. 278). Grey cast iron leaves a residue consisting partly of graphite, partly of a carbonaceous substance similar to that obtainable from white cast iron, and, partly of a black carbonaceous substance which is magnetic, takes fire by contact with the air, and leaves when burnt a residue of ferric oxide.

Cast iron is slowly acted upon by sea-water. Cannon balls that had been lying in the sea off the coast of Normandy since 1692, were found to have lost two-thirds of their original weight, contained no metallic iron, and were converted into a substance that could be cut with a knife (Deslongchamps, J. Chim. méd. xiii. 89). Cannon balls taken from vessels sunk fifty years before, near Carlscrona, were found to be partly converted into a grey porous graphite substance, which after exposure to the air for a quarter of an hour, became so heated that the adherent water was converted into steam (Berzelius, *Gmelin's Handbook*, v. 218). The substance remaining after the action of sea-water, appears to be similar to that remaining, mixed with graphite and the bulky carbonaceous residue, after dissolving grey cast iron by dilute hydrochloric acid, and which Karsten regards as a compound of iron with three equivalents of carbon. Berzelius considered this solution of cast iron by sea-water to be due to the conjoint action of carbonic acid and oxygen. The solution of cast iron takes place at places where it is exposed to the combined influence of fresh water and sea-water by tides more rapidly than in sea-water. (Mallet, *op. cit.*)

The solution of cast iron takes place at places where it is exposed to the combined influence of fresh water and sea water, by tides more rapidly than in sea water.

The maximum amount of carbon in cast iron is met with in specular iron, varying from 5·75 to 5·24 per cent. Bromeis and Percy consider that the manganese present, so far as is yet known, in all specular iron containing as much as 5 per cent. carbon, is in some way essential to this high proportion of combined carbon.

In grey cast iron the amount of carbon varies, as a general rule, between 2 and 4·65 per cent.; in white cast iron it is from 3·5 to 5·75 per cent; but the difference between white and grey cast iron is more intimately connected with the state in which the carbon exists, than with the amount of this substance.

Analyses of cast iron.

Ore used	Spathic iron ore			Magnetic iron ore		Franklinite	Specular and brown iron ore	
Fuel used	Charcoal							
Source	Styria	Müsen	Bohemia	Dannemora		New Jersey	Nova Scotia	India Iron Co.
Analyst	Widtermann	Fresenius	Richter	Henry		Henry	Tookey	W.A.
Kind of iron	Specular iron						No. 1 grey	grey pig
Iron	94·68	82·860	. .	92·906	95·57	81·363	94·85	
Carbon, combined	3·88	4·323	2·311	4·809	4·20	6·900		
Carbon, graphitic	. .	. .	. .	. .	. .	. .	3·50	3·38
Silicon	0·41	0·997	2·732	0·176	0·08	0·100	0·84	0·44
Sulphur	0·02	0·014		trace	trace	*0·187	0·02	0·04
Phosphorus	0·04	0·059		0·122	0·05	. .	0·19	0·27
Manganese	0·98	10·707	22·183	1·987	0·10	11·500	0·44	0·14
Copper	. .	0·066						
Aluminium	. .	0·077						
Calcium	0·07	0·091						
Magnesium	0·01	0·045						
	100·04	99·954	100·00	100·00	100·00	100·00	99·84	
	1	2	3	4	5	6	7	8

Ore used	Clay iron ore of coal measures							Northampton clay iron ore and roasted tap cinder
Iron in ore	39·8			—		—	—	
Sulphur in ore	trace			—		—	—	
Phosphorus in ore	0·50			—		—	—	
Fuel used	Thick-coal coke			—		—	—	
Sulphur in fuel	0·50			—		0·31	—	—
	Staffordshire							
Name of works	Lays; Dudley			Level; Dudley		Netherton	Goldendale	Russell's Hall
Analyst	Woolwich Arsenal							Henry
Kind of iron	hot blast		grey pig cold blast		hot blast	forge pig cold blast		No. 4 forge hot blast
Iron	. .	. .	. .	. .	. .	. .	. .	92·82
Carbon, combined	. .	. .	. .	. .	. .	. .	. .	0·19
Carbon, graphitic	2·87	3·34	3·21	2·56	2·61	2·81	2·54	2·45
Silicon	1·16	1·18	1·54	1·75	1·40	0·57	2·71	2·07
Sulphur	0·08	0·07	0·07	0·05	0·04	0·06	0·04	*0·32
Phosphorus	. .	0·55	0·23	0·63	0·72	0·29	1·07	1·43
Manganese	. .	. .	. .	0·06	0·49	0·13	0·98	0·72
Aluminium	. .	. .	. .	. .	. .	. .	. .	trace
Arsenic	. .	. .	. .	. .	. .	. .	. .	trace
	9	10	11	12	13	14	15	16

Ore used	Clay iron ore of coal measures							
Phosphorus in ore	—		—		0·41	0·73	—	
Fuel used	Barnsley coal		Deep hard coal and coke		Brand's hard coal		—	
Sulphur in fuel	0·65		—		0·52		—	
Name of works	East End; Wellingbro'; *Northamptonshire*		West Hallam		Butterley		Bowling; *Yorkshire*	
			Derbyshire					
Analyst	Woolwich Arsenal.							
Kind of iron	cold blast		hot blast		hot blast		—	
	No. 1 grey	mottled pig	forge pig	foundry	No. 2 pig	No. 4 pig	No. 1	No. 3
Iron								
Carbon, graphitic	2·85	2·10	2·57	2·40	2·74	2·60	2·90	2·80
Silicon	1·92	2·11	1·53	1·50	2·36	1·34	1·94	1·51
Sulphur	0·10	0·13	0·05	0·06	0·02	0·11	0·04	0·06
Phosphorus	1·19	1·07	0·70	0·34	1·21	0·75	0·57	0·44
Manganese	0·24	0·08	0·94	0·60	1·06	0·40		
	17	18	19	20	21	22	23	24

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* Probably estimated too high. See *Estimation of Sulphur*, p. 372.

Analyses of cast iron—continued.

Ore used	Clay iron ore		Hæmatite	Hæmatite			Cleveland ore No. 4	No. 5
Iron in ore	—		—	69·1				
Sulphur in ore	—		—	—				
Phosphorus in ore	—		—	trace				
Fuel used	—		charcoal	coke			coke	coke
Sulphur in fuel	—		—	1·09			1·05	0·91
Name of Works	**Beeston** *Yorkshire*		**Newland** *Lancashire*	Hæmatite Co^{y}., **Whitehaven**; *Cumberland*			**South Bank** *Durham*	**Stockton on Tees**
Analyst	Woolwich Arsenal							
Kind of iron	cold blast No. 3 pig	No. 4 pig		hot blast ? No. 1 pig	No. 2 pig	No. 4 pig	hot blast No. 2 pig	No. 3 pig
Iron								
Carbon combined	. .	. .	. .	. .	little	0·35		
Carbon graphitic	2·83	2·76	2·83	3·22	2·24	1·86	3·04	3·31
Silicon	2·17	1·80	0·59	3·02	2·77	2·63	2·73	1·43
Sulphur	0·05	0·84	0·03	. .	0·01	0·10	0·04	0·03
Phosphorus	0·55	0·55	0·10	0·06	0·05	0·08	1·30	1·36
Manganese	1·00	0·61	. .	0·11	0·07	0·07	0·38	0·06
	25	26	27	28	29	30	31	32

Ore used	Spathic iron ore					Clay iron ore		
Iron in ore	33·56—49·78					—		
Sulphur in ore	traces					—		
Phosphorus in ore	traces					—		
Fuel used	Coke							
Sulphur in fuel	0·60							
Name of works	*Durham* **Weardale Co.**			**Tow Law**		*Scotland* **Calder**	**Clyde**	
Analyst	W. A.			Riley	Tookey	Berthier		
Kind of iron	No. 1. pig	No. 2 pig	No. 3 pig	No. 1 pig	specular iron	foundry pig		white pig
Iron	. .	. .	. .	90·584	. .	94·63	92·30	92·24
Carbon combined	. .	. .	. .	. .	4·100	1·20	0·40	0·30
Carbon graphitic	3·24	2·26	2·15	2·795	. .	1·40	1·80	1·52
Silicon	1·80	4·25	1·18	4·414	0·230	1·53	2·80	1·79
Titanium	. .	. .	. .	trace				
Sulphur	0·04	0·06	0·12	0·039	0·030	0·35	1·40	0·60
Phosphorus	0·19	0·07	0·19	0·099	0·073	0·39	1·30	0·95
Manganese	1·45	1·04	trace	1·837	2·370	0·50	. .	2·60
Nickel, cobalt, copper and lead	. .	. .	. .	traces	0·014			
	33	34	35	36	37	38	39	40

Ore used	Clay iron ore of coal measures						Brown iron ore	
Iron in ore	—		—			56·53	—	
Sulphur in ore	—		—			—	—	
Phosphorus in ore	—		—			0·32	—	
Fuel used	—		Three-quarter coal coke			coke	coke	
Sulphur in fuel	—		0·74			0·76	0·90	
Name of works	**Dowlais**		**South Wales** **Blaenavon**			**Pontypool**	**Park End**; *Dean Forest*	
Analyst	Riley		Woolwich Arsenal					
Kind of iron	cold blast No. 3	white pig	cold blast No. 3 pig	No. 1 pig	forge pig	cold blast grey pig	cold blast No. 1 pig	grey forge
Iron	94·56	95·10						
Carbon combined	0·04	2·84	. .	. .	2·37			
Carbon graphitic	3·10		2·64	3·40		2·53	3·26	3·08
Silicon	2·16	1·21	1·68	1·36	1·09	1·23	2·34	2·18
Sulphur	0·11	0·46	0·08	0·07	0·73	0·08	0·04	0·06
Phosphorus	0·63	0·64	0·27	0·29	0·76	0·46	0·14	0·14
Manganese	0·50	0·14	0·66	0·28	0·22	0·42	0·23	0·14
Nickel and cobalt	0·05	0·03						
	41	42	43	44	45	46	47	48

Besides iron and carbon, cast iron always contains other substances, as indicated by the above analyses, especially silicon, sulphur, phosphorus, manganese, arsenic, copper. They probably exist, in combination with equivalent quantities of iron, as silicide, sulphide, phosphide, &c., and some of them appear to exercise considerable influence upon the quality and characters of the metal, although the mode in which it is exercised is but very partially understood, and the very nature of that influence is in some cases dubious.

Silicon is almost always present in cast iron to some extent, originating from the deoxidation of silica in the process of smelting. The amount varies very much. In white cast iron it is generally from 0·1 to 0·5 per cent. In grey cast iron the amount is much greater, and is seldom less than 0·5 per cent., sometimes exceeding even 3 per cent. Karsten found 3·46 per cent. to be the maximum amount. The greater amount of silicon in grey cast iron is considered to be due to the higher temperature at which it is produced. Iron produced with hot blast contains more silicon than that produced with cold blast.

It is generally considered that, within the ordinary limits as to the amount of silicon in cast iron, this substance does not exercise any prejudicial influence upon the quality of the metal; but, in the conversion of cast iron into malleable iron, the silicon must be as much as possible separated, since it is very detrimental to malleable iron as regards its tenacity. The greater the amount of silicon in pig iron, the greater also is the waste incurred in its conversion into malleable iron by the puddling operation.

Sulphur is almost always present in cast iron, but sometimes the amount is so small that it can hardly be estimated. It probably never reaches 0·5 per cent. in good cast iron. Iron smelted with mineral fuel always contains more sulphur than that smelted with charcoal, in consequence of the sulphur contained in the coal or coke being transferred to the iron. The presence of sulphur in cast iron renders it more fusible, but also more liable to solidify sooner when slightly cooled below the melting point, so as to become quite viscid while still red-hot.

When specular iron is melted with sulphur, carbon separates and collects upon the surface of the melted mass in the form of graphite, which differs from ordinary graphite in having no lustre. Grey cast iron melted with sulphur is converted into white cast iron, containing a greater amount of carbon than the original grey iron, as shown in the following results obtained by Karsten (*Eisenhüttenkunde*, i. 583):

	The grey cast iron contained in 100 pts.	The resulting white iron contained in 100 pts.
Combined carbon	0·6253	5·4878
Graphite	3·3119	
Sulphur	0·0286	0·4464

Hence it would appear that sulphur displaces carbon existing in combination with iron, but that up to a certain point, the carbon so displaced from combination with one portion of the iron, enters into combination with another portion, until no more can be taken up. The presence of sulphur in cast iron appears therefore to determine the existence of the carbon in the state of combination with the iron, and thus to be conducive to the production of white cast iron. (Janoyer, Ann. des Mines, 1851, iv. 20; Weston, *Percy's Metallurgy*, ii. 135.)

Phosphorus is frequently present in cast iron, sometimes to the extent of 1 or 2 per cent. When amounting to more than 0·5 per cent., it renders the iron brittle but more fusible, very liquid when melted, and capable of remaining longer in the liquid state. Within certain limits, therefore, the presence of phosphorus in iron intended for casting, is advantageous rather than otherwise.

Nitrogen.—It appears that cast iron sometimes contains a minute amount of nitrogen, and that it has a considerable influence on the character of the metal. Schafhäutl estimated the nitrogen in several kinds of cast iron as follows (Prechtl, Techn. Encyklop. 1847, xv. 364; Phil. Mag. 1840, xvi. 44):

White cast iron (Maesteg, South Wales)	0·764 per cent.
Grey cast iron (Creuzot, France)	0·720 „
Specular iron	1·200 „

Marchand's experiments led him to doubt the existence of nitrogen in cast iron; and to infer that if it were present, it never amounted to 0·02 per cent., and that the indications of nitrogen obtained by analysis were generally referable to absorption of atmospheric nitrogen by the iron, and formation of cyanogen during the analysis.

Bouis (Compt. rend., 1861, lii. 1195) on the contrary, considers that nitrogen is often present in cast iron, and has estimated the amount in a sample of very hard white cast iron, containing much manganese, at 0·15 per cent. This subject, however, is far from having been satisfactorily investigated.

Arsenic.—There is much difference of opinion as to the influence of arsenic upon cast iron, and as to the frequency of its presence, but there are some well-established instances of cast iron containing a considerable amount of arsenic. Wöhler found it in four samples of pig iron, and Schafhäutl has stated that pig iron made at Alais from arsenical ore, contained from 2·5 to 4 per cent. of arsenic. Karsten never detected arsenic in pig iron. According to Berthier's analyses of some iron shells and shot from Algiers, they contained from 9·8 to 27 per cent. arsenic, constituting in fact a true alloy, and more recently a wrought shot from Sinope has been found to contain 16·20 per cent. arsenic by Dr. Noad. (Percy, *Metallurgy*, ii. 76.)

The presence of small amounts of arsenic in cast iron, is considered to have the effect, like phosphorus, of rendering the metal more fusible, brittle, and weaker.

Titanium appears to be frequently present in some kinds of cast iron, and it has been supposed to improve the quality of the metal. Several patents have been obtained for introducing it into cast iron intended for the manufacture of steel (Mushet, 13 specifications, March 1859 to December 1861), but it is very questionable whether this "invention" has any real foundation of known fact. The following analyses of titaniferous pig iron are by Mr. Riley.

Ore used	Hæmatite and 7·57 % Ilmenite.	The same, with some Belfast aluminous ore.		Cornish ⅓, hæmatite ⅓, and Irish bog-ore ⅓, containing 6 to 9 per cent. manganese.		Cornish ⅔, Irish bog-ore ⅓.
Kind of Iron	No. 1 foundry pig.	No. 2 pig.	grey pig.			
Iron	93·47	92·79	92·04	87·90	86·88	84·26
	. .	. .	. .	0·31	1·02	0·07
Carbon . . .	3·31	3·18	3·11	3·12	3·01	2·61
Silicon . . .	1·86	3·28	3·55	2·59	2·55	3·32
Titanium . . .	1·15	0·71	0·47	0·79	1·15	1·63
Sulphur . . .	0·06	0·06	0·11	0·03	0·03	0·02
Phosphorus . .	0·08	0·06	0·09	0·15	0·15	0·20
Manganese . .	0·50	0·48	1·09	5·85	6·37	8·09
Nickel and cobalt .	. .	. .	. .	0·06	0·11	
Copper and antimony .	. .	. .	. .	0·06	0·04	0·06
	100·437	100·56	100·46	100·85	100·31	100·27

Vanadium has also been found in the pig iron made from the ores of Taberg in Sweden (Sefström, Berz. Jahresb. 1832, xi. 97), and in pig iron made from the Seend ore of Wiltshire. (Riley, Journ. Chem. Soc. [2] ii. 21.)

Chromium has been found in cast iron, but there is no evidence to show whether it has any influence on the character of the metal.

Manganese is very frequently present in cast iron, and it appears to have some influence in determining a high degree of carburation of the iron, as well as the existence of the carbon in a state of combination with the iron, so that its presence in the materials smelted, tends to effect the production of white cast iron (See *ante*, p. 331). Cast iron containing manganese appears to be especially suited for the production of steel or steely iron. (See STEEL.)

Copper is not unfrequently present in cast iron. When exceeding 0·2 per cent. it is said to render the metal harder, tougher, and stronger.

Zinc is sometimes present in cast iron smelted from ores containing zinc; and Karsten found cast iron containing traces of zinc to be very soft, but rotten and brittle. (*Eisenhüttenkunde*, i. 519.)

Aluminium, *Magnesium*, *Calcium* and *Potassium* are sometimes indicated by analyses as existing in minute proportion in some kinds of cast iron, but scarcely anything is known of their influence on the characters of the metal.

Occurrence. Although iron is one of the most abundant and widely distributed of the heavy metals, it is very seldom met with naturally in the metallic state. There are two species of native metallic iron, viz. telluric and meteoric iron.

1. *Telluric iron* is very rare; it occurs massive in plates and grains, is more malleable and ductile than ordinary iron; its specific gravity is from 7· to 7·8. It has been found associated with brown hæmatite and quartz in a lode near Grenoble (Schreiber, Journ. de Phys. July 1792); at Canaan, Connecticut, as a vein two

inches broad in mica slate (Shepard). This specimen contained 91·8 per cent. iron iron and 7 per cent. carbon. It is said to be mixed with the granular platinum of South America (John), and disseminated through some basaltic rocks (Andrews), also in the auriferous sand of Oláphian (Molnar). Native iron containing 6 per cent. of silicon and a little sulphur is said to have been found with galena, in the lodes at Leadhills, and in volcanic scoriæ at Gravenière in Auvergne.

2. *Meteoric iron* is met with, both as large compact masses, and as grains and splinters disseminated through earthy meteorites. Its colour is somewhat like that of platinum, and it is characterised by always containing nickel, sometimes also cobalt, copper, chromium and tin. The masses of meteoric iron found in South America and Siberia, and estimated to weigh several tons, are among the most remarkable that are known. Meteoric iron almost always contains particles of iron sulphide mixed with it, apparently neither magnetic nor ordinary pyrites. (Rammelsberg, Pogg. Ann. 1849, lxxiv. 442.)

Analyses of Meteoric Iron.

Fell at . .	Bohumilitz, Bohemia, in 1829.	Krasnojarsk, Siberia —	Hraschina, Croatia, 1751.	Cape, Africa. —	Clairborne, Alabama. —	Potosi. —	N. America. —	Bitburg, near Treves. —
Weight . .	103 lbs.	1600 lbs.	71 lbs.	300 lbs.	—	—	—	3300 lbs.
Analyst . .	Berzelius.		Wehrle.		Jackson.	Morren.	Silliman & Hunt.	Stromeyer.
Iron . . .	93·78	88·04	89·78	85·61	66·56	83·57	92·58	81·8
Nickel . . .	3·81	10·73	8·89	12·27	24·71	12·67	5·71	11·9
Cobalt . . .	0·21	0·46	0·67	0·89	. .	. .	. .	1·0
Copper . . .	. .	0·07	. .	. .	. .	. .	trace	
Manganese . .	. .	0·13	. .	. .	3·24	. .	. .	0·2
Chromium . .	. .	. .	. .	. .	trace			
Tin . . .	. .	trace						
Magnesium . .	. .	0·05						
Arsenic . .	. .	. .	. .	. .	. .	. .	trace	
Sulphur . .	. .	trace	. .	. .	4·00	. .	. .	5·1
Iron sulphide .	. .	. .	. .	. .	. .	2·30		
Carbon . .	. .	0·04						
Chlorine . .	. .	. .	. .	. .	1·48	0·91		
Insoluble . .	2·20	0·48	. .	. .	. .	. .	1·40	
	100·00	100·00	99·34	98·77	99·99	99·45	99·69	100·0

Iron ores. Compounds of iron occur native in great numbers as minerals, and very widely distributed; there are indeed few natural bodies in which iron is not present to some extent; it exists in the ashes of most plants (see i. 417, ii. 680), and appears to be an essential constituent of the blood of animals (see *ante*, p. 2). Of the native compounds containing iron in large proportion, those which occur in greatest abundance are the oxides, disulphide, carbonate, phosphate, titanate, and silicate. But for the extraction of the metal the only minerals that are suitable are the several oxides and the carbonate, all of which occur as large masses, of a greater or less degree of purity, being generally mixed with varying amounts of siliceous or earthy substances, and smaller quantities of various other minerals. The most important varieties of these ores of iron are the following:—

Native magnetic oxide, Magnetic iron-ore; Magneteisen; Oxyde magnetique.—This is the richest of the ores of iron available for smelting; in its purest state it contains 72·41 per cent. iron. It is black and generally has a metallic lustre, and occurs both crystalline, granular and compact or even earthy, at well as in the state of sand. It exists abundantly in many localities as beds or veins, and sometimes forming entire mountain masses, associated with volcanic or schistose rocks, and chiefly in Norway, Sweden, Siberia, and North America. It is sometimes largely mixed with pyrites and other sulphuretted minerals. In this country magnetic iron-ore occurs in the West of England and at Rosedale in Yorkshire.

The mineral known as *Franklinite* appears to be a variety of magnetic iron ore in which ferrous oxide is replaced by zinc oxide.

Analyses of Magnetic Iron Ore.

Source	Dartmoor.	Cornwall.		Rosedale.		Dannemora.	Franklinite.
Analyst	Riley.	Noad.		Northcutt.	Pattinson.	Karsten.	Rammelsberg.
Ferric oxide	62·20	44·40	66·50	12·22	32·67	70·23	64·51
Ferrous oxide	17·32	20·00	13·00	35·25	33·85	29·65	
Manganous oxide	0·14	0·16	·56	. .	0·69	. .	13·51
Zinc oxide	. .	. .	. .	. .	. .	. .	25·30
Alumina	3·81	5·20	3·60	14·10	3·15		
Lime	5·52	0·60	0·56	2·38	2·86		
Magnesia	1·82	1·00	1·52	3·95	1·59		
Potash and soda	0·10	. .	. .	. .	trace		
Silica	9·66	. .	. .	9·65	6·95		
Carbonic acid	. .	. .	. .	16·25	10·36		
Phosphoric acid	**0·10**	**0 50**	**0·57**	. .	**1·41**		
Sulphuric acid	. .	**0·04**	**0·04**	**trace**	**trace**		
Iron pyrites	**0·07**	. .	. .	**trace**	**0·03**		
Water combined	0·28	2·50	3·20	4·80	3·76		
Water hygroscopic	0·34						
Insoluble in acid	. .	24·20	9·40	. .	0·84		
	101·36	99·60	98·95	98·60	98·16	99·88	103·32
Percentage of iron	57·01	. .	. .	35·94	49·17	71·68	45·16

Native ferric oxide; Hæmatite, Red iron ore; Rotheisenstein; Fer oligiste.—In its purest state this ore consists entirely of anhydrous ferric oxide containing 70 per cent. iron. It occurs in various states, crystalline, massive, and earthy, very often as lumps with a radiating fibrous structure and smooth surface, known as "kidney ore." It also forms large veins or beds, associated with quartz, calcspar, and heavy spar. Some kinds are hard, others soft and friable, and it generally contains varying amounts of earthy admixtures. The principal British deposits of hæmatite are in Cumberland and

Analyses of Red Iron Ore.

Source	Whitehaven.		Ulverstone.		Cleator.	Ulverstone.	Whitchurch, South Wales.
Analyst	W.A.	Dick.	Spiller.	R. Smith	Dick.		Ratcliffe
Ferric oxide	98·71	95·16	94·23	90·94	90·55	86·50	66·55
Ferrous oxide	. .	. .	. .	. .	. .	. .	1·13
Manganous oxide	trace	0·24	0·23	0·25	0·10	0·21	1·13
Alumina	. .	0·06	0·63	trace	1·48	0·30	2·79
Lime	trace	0·07	0·05	0·99	0·71	2·77	9·40
Magnesia	. .	. .	trace	trace	0·06	1·46	1·39
Potash	. .	. .	. .	. .	. .	. .	0·42
Soda	. .	. .	. .	. .	. .	. .	0·15
Silica	1·00	5·66	4·90	6·68	7·05	6·18	8·90
Carbonic acid	. .	. .	. .	0·78	. .	2·96	5·73
Phosphoric acid	**trace**	**trace**	**trace**	**trace**	**trace**	**trace**	**1·02**
Sulphuric acid	. .	**trace**	**0·09**	**0·24**	**trace**	**0·11**	**1·31**
Iron pyrites	. .	**trace**	**0·03**				
Water hygroscopic	. .	. .	0·39	. .	. .	. .	2·12
Water combined	. .	. .	0·17	. .	. .	. .	
Organic substance	. .	. .	. .	. .	. .	. .	0·38
	99·71	101·19	100·72	99·88	99·96	100·49	102·42
Percentage of iron	**69·10**	**66·60**	**65·98**	**63·66**	**63·25**	**60·55**	**47·47**

Lancashire, the Isle of Man, Devonshire and Cornwall. On the Continent it occurs chiefly in the Hartz, Silesia, the Austrian provinces, and in Norway. A peculiar oolitic hæmatite occurs in the neighbourhood of Liége.

Red ochre is an earthy variety of ferric oxide containing a large admixture of clay.

Specular iron ore; Eisenglanz; Fer speculaire.—This also consists of anhydrous ferric oxide in a crystallised form. Its colour is iron grey or almost black. Specific gravity 4·8 to 5·3. The crystals of this mineral belong to the hexagonal system, R.oR and sometimes $R\,.\,\frac{4}{3}P^2\,.\,\frac{1}{4}R$. It occurs chiefly in schistose rocks, in Norway, the Erzgebirge, in Russia, and several parts of the South of Europe, the most extensive deposit being that in Elba, which has been worked upwards of 3,000 years.

Specular iron ore often contains titanium, either in the form of rutile, or combined with the ferric oxide constituting ilmenite. This was formerly considered prejudicial to the ore; but quite recently it has been stated that the presence of titanium in iron ores, contributes in some way, not yet understood, to the production of good iron.

Native hydrated ferric oxide; Brown iron ore; Brauneisenerz; hematite brun.—This ore consists essentially of hydrated ferric oxide, which in the pure state contains 59·89 per cent. of iron and 14·44 per cent. combined water. It is sometimes indistinctly crystalline or fibrous; but more generally compact or earthy, and of various shades of colour from blackish-brown to yellowish-brown. This ore frequently contains a considerable amount of manganese, and a more or less considerable admixture of foreign earthy substances. It occurs abundantly in the Forest of Dean in Gloucestershire, in several parts of Devonshire and Northamptonshire, and Lincolnshire, as well as in Weardale, Durham, where it has originated chiefly by the alteration of spathic iron ore. On the Continent it is very abundant, and is one of the principal ores smelted in France and Germany.

A variety of this mineral occurs in many places under the name of bog iron ore (*Sumpferz; minerai des marais*), which has apparently been formed by deposition from ferruginous water under the influence of living organisms. Some kinds of this ore furnish very good iron—for instance, the lake ores of Sweden and Lower Canada; but generally it contains so large an amount of phosphorus as to be useless for smelting.

Yellow ochre is an argillaceous variety of hydrated ferric oxide containing more combined water than brown iron ore, and basic sulphate; sometimes also basic silicate, phosphate, and arsenate.

Analyses of Brown Iron Ore.

Source	Dean Forest.			Devonshire.	Northamptonshire.		Weardale.	
Analyst	Dick.		Price.	Dick.	Dick.		Tookey.	Spiller.
Ferric oxide . .	90·05	89·80	89·28	89·39	76·00	74·82	72·08	49·57
Ferrous oxide . .	. .	. .	. .	. .	trace	. .	. .	10·77
Manganous oxide .	0·88	0·04	. .	0·33	0·40	0·57	6·60	3·06
Alumina . . .	0·14	0·98	. .	0·52	2·30	2·91	0·40	0·84
Lime . . .	0·06	0·51	. .	0·33	0·41	0·76	0·56	5·69
Magnesia . . .	0·20	0·40	. .	0·20	0·11	0·18	1·90	1·21
Potash . . .	. .	. .	. .	. .	. .		. .	0·05
Silica . . .	0·92	2·14	0·98	1·42	5·33	6·93	4·09	6·64
Titanic acid . .								
Carbonic acid . .	. .	. .	. .	. .	. .	0·57	0·13	14·49
Phosphoric acid .	0·09	0·13	trace	0·13	1·03	3·17	0·22	0·01
Sulphuric acid . .	traces	trace	. .	trace	. .	trace	. .	trace
Iron pyrites . .		. .	. .	trace	. .	0·96	. .	0·03
Water hygroscopic .	. .	. .	9·74	8·83	1·80	. .	12·40	1·81
Water combined .	9·22	7·05			12·40	11·89		6·63
Organic substance .	. .	. .	. .	. .	. .	trace	. .	trace
	100·76	101·05	100·00	101·15	99·78	100·46	99·38	100·80
Percentage of iron .	63·04	62·86	62·57	62·60	53·20	52·05	49·78	43·02

Analyses of Brown Iron Ore—continued.

Source	North-amptonshire.	Wales; Llantrissant.	Lincolnshire Brigg.	North-amptonshire.	Dorsetshire.	Wiltshire; Seend.	North-amptonshire.	Cornwall; St. Austle.
Analyst	Price & Nicholson.	Riley.	Tookey.	Percy.	Tookey.	Riley.	Spiller.	Riley.
Ferric oxide . .	68·58	59·05	58·10	56·20	55·21	53·48	52·86	51·87
Ferrous oxide . .	. .	. .	. .	trace	. .	. .	trace	
Manganous oxide .	0·36	0·09	0·88	0·20	0·95	1·60	0·51	0·43
Alumina . . .	3·27	trace	4·95	2·43	7·70	4·38	7·39	4·01
Lime . . .	0·66	0·25	4·15	0·49	0·70	0·84	7·46	0·52
Magnesia . . .	. .	0·28	0·96	0·17	1·15	0·72	0·68	0·17
Silica . . .	11·63	34·40	11·70	29·07	19·65	26·23	13·16	36·03
Carbonic acid . .	. .	. .	1·08	. .	. .	trace	4·92	
Phosphoric acid .	0·97	0·14	1·40	0·84	0·42	0·87	1·26	0·49
Sulphuric acid . .	0·18	. .	. .	. .	0·16			
Iron pyrites . .	. .	0·09	. .	. .	. .	trace	·0·03	0· 3
Water { hygroscopic .	11·56	0·24	16·46	1·16	13·11	13·61	. .	0·80
Water { combined .		6·14		9·74			11·37	5·80
Organic substance .								
	100·26	100·68	99·68	100·30	99·05	101·73	99·54	100·15
Percentage of iron .	48·00	41·34	40·67	39·34	38·65	37·44	37·00	36·31

Analyses of Brown Iron Ore—continued.

Source	North-amptonshire.	Oxfordshire; Woodstock.	Dean Forest.	Staffordshire; Froghall.	North-amptonshire.	Dean Forest.	Belfast.	North-amptonshire.
Analyst	Dick.	Tookey.	Dick.		Riley.	Dick.	Tookey.	Riley.
Ferric oxide . .	38·04	44·67	32·76	52·83	50·53	48·99	35·91	34·41
Ferrous oxide . .	10·54	0·86	. .	. .	trace	0·24	6 57	trace
Manganous oxide .	0·69	0·44	trace	0·81	0·51	0·16	0·05	0·27
Alumina . . .	13·02	9·10	0·05	. .	7·52	0·17	27·95	6·40
Lime	trace	9·29	0·25	14·61	11·92	14·07	0·60	25·72
Magnesia . . .	4·35	0·66	0·25	5·70	0·62	10·21	0·20	0·87
Potash . . .	0·38	. .	. .	. .	0·11	. .	0·49	
Silica . . .	23·24	12·34	63·52	trace	8·80	0·79	9·75	6·69
Carbonic acid . .	0·16	6·11	. .	18·14	7·98	20·75	. .	18·45
Phosphoric acid .	0·26	0·55	0·0 9	0·32	1·28	0·06	. .	1·47
Sulphuric acid . .	trace	. .	trace	0·28	. .	trace	. .	0·07
Iron pyrites . .	0·13	trace		. .	0·17	. .	. .	0·30
Water { hygroscopic .	. .	16·31	. .	. .	11·00	. .	18·60	6·97
Water { combined .	6·92		3·55	4·75		5·18		
Organic substance .	0·19	. .	. .	1·30				
	99·92	100·33	100·47	98·74	100·44	100·62	100·12	101·62
Percentage of iron .	34·83	31·94	22·93	36·98	35·37	34·46	30·25	24·09

Native ferrous carbonate; Spathic iron ore; Spatheisenstein; fer spathique.—This mineral consists essentially of ferrous carbonate, and in its purest state contains 48·27 per cent. of iron. It is generally crystalline, sometimes presenting distinct crystals (see i. 785), and sometimes in the form of fibrous nodular masses known by the name of sphærosiderite. It varies in colour from white to yellow or brown, and is very often found to have undergone more or less complete conversion into hydrated ferric oxide under the influence of atmospheric oxygen. Spathic iron ore occurs as veins and beds in the older rocks, and associated with limestone strata. It is worked in this country chiefly in Durham and Somersetshire; on the Continent it is of more frequent occurrence, the chief localities being Styria and Westphalia, where it constitutes entire mountains, and has long been famous under the name of "steel ore" for yielding very fine qualities of iron and steel.

Spathic iron ore generally contains a considerable amount of manganese and small quantities of lime and magnesia, and is sometimes associated with lead and copper ores, quartz, fluor-spar, calcspar, heavy spar, &c., but is frequently quite free from any admixture of impurities that would be prejudicial to the iron made from it.

Analyses of Spathic Iron Ore.

Source	Müsen, Westphalia.	Ripsey Vein. Durham.	Weardale. Durham.	Brendon, Somersetshire.		Siegen Alte Birke.	Ehrenfriedersdorf; Saxony.	Exmoor; Devon.
Analyst	Peters.	Dick.	Tookey.	Spiller,	Price & Nicholson.	Schnabel.	Magnus.	Spiller.
Ferric oxide . .	2·75	. .	0·81	0·81	. .	. .	. .	0 07
Ferrous oxide . .	. .	49·47	49·77	43·84	43·94	43·59	36·81	17 91
Manganous oxide .	0·83	2·42	1·93	12·64	12·88	17·87	25·31	7·64
Zinc oxide . . .	0·04							
Alumina . . .	1·63	0·06	. .	0·01				
Lime . . .	1·75	3·47	3·96	0·28	. .	0·88	. .	24·80
Magnesia . . .	2·29	3·15	2·83	3·63	4·00	0·24	. .	6·17
Silica . . .	1·62	4·93	3·12	0·07				
Carbonic acid . .	39·92	37·71	37·20	38·86	39·18	38·22	38·35	41·75
Phosphoric acid .	0·54	trace	trace	. .	. .	. .	. .	trace
Sulphuric acid . .	. .	trace						
Iron pyrites . .	0·22	. .	0·04	. .	. .	. .	. .	0·11
Water { hygroscopic .	0·45	. .	0·30	0·18	. .	. .	. .	0·38
Water { combined .								
Organised substance .	0·39	trace						
	100·55	101·29	99·96	100·32	100·00	100·00	100·47	99·23
Percentage of iron .	42·59	38·56	38·95	34·67	34·18	33·90	28·63	13·98

Ferrous carbonate mixed with clay often occurs with beds of coal, in sedimentary rocks, and is known under the name of argillaceous, sphærosiderite, or clay iron ore. It is compact and earthy; of various shades of grey and brown, or sometimes quite black, owing to an admixture of carbonaceous substance, and occurs in lenticular masses or nodules. This ore is generally very abundant in the coal measures; but in some instances it is almost wholly wanting in those rocks, as for instance in the coal fields of Northumberland, Durham, Lancashire, and Belgium. The principal localities where it is worked in this country are the coal fields of Scotland, Staffordshire, Shropshire and Wales.

It is found to some extent in France and Germany, and abundantly in America, but is not worked there.

Analyses of Clay Iron Ore from the Coal Measures.

	Scotland.							
Name of ore	Black band.							
Analyst	Colquhoun.							
Ferric oxide . .	. .	0·33	1·16	0·23	0·47	1·16	0·23	2·72
Ferrous oxide . .	45·84	38·80	35·22	53·03	43·73	35·22	53·82	40·77
Manganous oxide .	020	0·07						
Alumina . . .	2·53	6·20	5·34	0·63	5·13	5·34		
Lime	1·90	5·30	8·62	3·38	2·10	8·62	1·51	0·90
Magnesia . . .	5·90	6·70	5·19	1·77	2·77	5·19	0·28	0·72
Silica . . .	7·83	10·87	9·56	1·40	9·70	9·56	2·00	10·10
Carbonic acid . .	33.63	30·76	32·53	35·17	32·24	32·53	34·39	26·41
Sulphur . . .	. .	0·16	0·62	. .	0·20	0·62		
Water { hygroscopic .								
Water { combined .	. .	. .	. .	. .	. .	. .	. .	1·00
Organic substance .	1·86	1·87	2·13	3·63	1·50	2·13	7·70	17·38
	100·37	101·00	100·37	. .	99·66	100·37	100·00	100 00
Percentage of iron .	28·40	30·00	28·40	40·90	34·00	28·40	41·60	34·60

A variety of this ore containing from 10 to 15 or even 30 per cent. of coaly substance, occurs as thin layers in the coal measures of Scotland, and some parts of England and Wales, and is known under the name of "black band."

Analyses of Clay Iron Ore from the Coal Measures—continued.

	Yorkshire.			Derbyshire.			Staffordshire.	
Source	Black bed; Low-moor.	White mine; Parkgate.	Black mine;	Brown Rake; Butter-ley.	Dale-moor Rake; Stanton.	Dog-tooth; Stave-ley	Chalky mine; Foley.	Red Shag; Shelton.
Analyst	Spiller.						Dick.	
Ferric oxide . .	1·45	1·69	2·39	1·49	3·49	1·42	0·12	0·05
Ferrous oxide . .	36·14	39·38	41·77	37·99	39·55	28·27	51·07	46·53
Manganous oxide .	1·38	0·95	1·13	1·51	1·50	1·02	2·36	2·54
Alumina . . .	6·74	6·42	4·79	5·57	5·45	2·21	2·47	1·22
Lime	2·70	2·26	2·55	4·59	3·38	13·94	1·74	2·44
Magnesia . . .	2·17	3·89	3·85	3·37	2·88	9·27	1·10	1·39
Potash . . .	0·65	0·37	0·43	0·55	0·48	0·16	0·28	20
Silica	17·37	12·16	8·93	10·04	10·22	3·55	3·02	1·93
Carbonic acid . .	26·57	29·38	31·39	29·92	28·63	37·61	33·63	30·77
Phosphoric acid . .	0·34	0·47	0·75	0·80	1·12	0·74	1·12	0·69
Sulphuric acid . .	trace	. .	trace	trace	trace	trace	trace	0·04
Iron pyrites . .	0·10	trace	. .	0·06	0·05	0·04	0·17	0·34
Water { hygroscopic .	0·61	0·68	0·55	0·74	0·51	0·18	0·99	1·47
Water { combined .	1·16	1·41	1·15	1·47	1·24	0·73		
Organic substance .	2·40	0·54	0·86	1·42	1·14	0·92	1·24	10·46
	99·78	99·60	100·54	99·52	100·14	100·16	98·97	100·07
Percentage of iron .	29·12	31·82	34·16	30·60	33·20	22·98	39·88	36·39

Analyses of Clay Iron Ore from the Coal Measures—continued.

	Staffordshire.							
Source .	Dudley.					Bun-ker's Hill.	Darlaston.	
Name of ore	Pins.	Grains.	Gubbin.	White-stone.	Binds.	Balls.	White-stone.	Gubbin.
Analyst .	Dick.			Spiller.		Dick.	Tookey.	
Ferric oxide . .	0 54	0·13	0·40	0·04	1·15	0·43	3·17	3·82
Ferrous oxide . .	45·35	46·30	45·86	48·63	30·96	52·04	33·92	49·40
Manganous oxide .	0·56	1·44	0·96	1·29	0·73	0·92	0 77	0·86
Alumina . . .	5·70	4·80	5·86	3·64	9·58	4·98	6·44	3·05
Lime . . .	2·60	0·76	1·37	4·45	1·84	0·53	2·65	0 86
Magnesia . . .	1·26	0·94	1·85	0·80	3·11	1·18	4 43	0·52
Potash . . .	0·36	. .	. .	0·11	0·74	0·32	0·74	0·30
Silica . . .	10·63	10 29	10·88	6·21	26·50	6·63	18·23	6·22
Carbonic acid . .	30·21	30·44	31·02	32·16	22·13	32·31	26·89	32·05
Phosphoric acid .	0·46	0·74	0·21	0·31	0·26	0·21	0·35	0·23
Sulphuric acid . .	trace	trace	trace	0·06	trace	trace		
Zinc sulphide . .	. . .	. .	. .	. .	. . .	. .	. .	1·27
Iron pyrites . .	0·20	0·07	0·10	0·16	0·12	0·13	0·15	0·13
Water { hygroscopic .	1·64	1·38	1·08	0·32	0·56	0·46	0·42	0·37
Water { combined .				1·23	1·83		0·98	0·29
Organic substance .	1·59	1·14	0·90	0·28	0·10	0·51	0·47	0·54
	100·99	98·43	100·29	99·69	99·61	100·25	99·61	99·81
Percentage of iron .	35·74	36·14	35·99	37·45	24·88	40·84	28·87	41·06

Analyses of Clay Iron Ore from the Coal Measures— continued.

	South Wales.							
Source .	Pontypool.	Blaenavon.	Cwm Avon.	Aberdare.		Abercarn.	Llanelly.	
Name of ore	Balls.	Black pin.	Sulphury mine.	Coal brass.		Black band.		
							raw.	calcined.
Analyst .	Riley.	Dick.		Price & Nicholson.		Ratcliffe.	Price.	
Ferric oxide . .	0·50	0·45	0·34	. .	. .	4·10	. .	80·00
Ferrous oxide . .	44·50	41·22	40·30	37·07	42·64	43·37	43·30	
Manganous oxide .	0·73	1·07	1·03	0·23	0·26	1·50	1·08	1·80
Manganic oxide .	. .	. .	. .	. .	. .		. .	
Lime . . .	2·05	2·89	1·44	6·61	5·24	3·00	1·26	2·10
Magnesia . .	3·26	3·68	2·94	7·40	5·26	0·25	2·67	4·45
Soda . . .	0·13							
Potash . . .	. .	0·48	0·82	. .	. .	0·32		
Alumina . . .	5·95	4·88	7·90	. .	. .	6·5		
Clay . . .	. .	. .	. .	2·70				
Silica . . .	10·81	11·60	14·43	. .	. .	·80	7·20	10·61
Carbonic acid . .	30·92	30·07	28·23	37·14	36·89	30·50	28·46	
Phosphoric acid .	0·23	0·76	. .	0·23	0·17	trace	0·67	1·03
Sulphuric acid . .	. .	trace	trace					
Sulphur . . .	. .	. .	. .	. .	. .	1·56	0·26	
Iron pyrites . .	0·11	0·15	0·09	trace	0·22	. .		
Water { hygroscopic .	0·76	. .	0·74	. .	. .	0·27		
Water { combined .		1·21	. .	. .	. .	0·31		
Organic substance .	0·21	0·82	0·29	9·80	8·87	6·25	15·10	
	100·24	99·28	99·43	100·18	99·55	100·28	100·00	99·99
Percentage of iron .	34·96	32·44	31·63	28·88	33·17	36·4	33·68	56·00

Clay iron ore also occurs abundantly in strata belonging to the Lias, as well as in the Oolite and Tertiary series of rocks, sometimes partially or wholly converted into brown iron ore by atmospheric oxidation. This ore is now largely worked in the Cleveland district in Yorkshire.

Analyses of Clay Iron Ore from the Lias and Oolites.

Source	Middlesbro.	Hutton Low Cross.	Eston Nab.	Upleatham.	Belmont	Grosmont.	Normanby.	Northamptonshire.
Analyst	Percy.	Crowder.	Crowder.	Crowder.	Percy.	Percy.	Pattinson.	Dick.
Ferric oxide . .	2·86	4·25	1·20	5·80	3·50	. .	2·60	3·31
Ferrous oxide . .	43·02	40·86	43·35	38·25	39·00	40 77	38·06	33·29
Manganous oxide .	0·40	. .	. .	. .	1·30	0·67	0·74	1·11
Alumina . . .	5·87	3·44	9·88	12·20	7·46	1·32	5·92	7·89
Zinc	5·14	3·80	0·58	5·00	7·44	4·08	7·77	0·50
Magnesia . . .	5·21	3·70	5·35	2·40	3·82	5·34	4·16	11·77
Potash . . .	. .	. .	. .	. .	. .	. .	. .	0·20
Silica . . .	7·17	7·20	7·65	7·45	9·46	8·80	10·36	19·49
Carbonic acid . .	25·50	32·50	22·96	25·40	23·06	31·80	22·00	24·79
Phosphoric acid .	1·81	0·96	3·87	0·50	1·60	0·06	1·07	0·22
Sulphuric acid . .	. .	0·30	. .	trace	. .	. .	trace	trace
Iron pyrites . .	. .	1·60	0·09	trace	. .	. .	0·14	0·13
Water { hygroscopic .	0·34	1·45	5·07	3·00	3·66	2·70	4·45	. .
Water { combined .	3·14							0·54
Organic substance .	0·15	. .	. .	. .	. .	. .	. .	0·08
	100·61	100·06	100·00	100·00	100·30	99·10	97·27	100·32
Percentage of iron .	35·46	34·75	34·54	33·81	32·78	31·71	31·42	28·28

Both clay iron ore and carbonaceous iron ore are frequently accompanied by admixtures of metalliferous, sulphuretted, arsenical, and phosphatic minerals, sometimes in such amount as to detract from their value for smelting purposes; but generally they are sufficiently pure to furnish iron of good quality. Some kinds of the ore known as "coal brass" also contain a considerable amount of ferrous carbonate, though they were disregarded as iron ores, until attention was directed to their composition in 1853 by Messrs. Price and Nicholson.

Native iron Sulphides occur very frequently and in great abundance in some places. Of late years these minerals have been much used as a source of sulphur, and are largely imported from Spain and Norway for that purpose. The principal varieties are:

1. *Iron pyrites* (*Eisenkies; pyrite*), which has a yellow colour and metallic lustre. Specific gravity 4·9 to 5·1. It occurs crystalline, granular and compact, frequently disseminated through other minerals. In its purest state it contains 53·33 per cent. iron, and 46·67 per cent. sulphur.

Analyses of Iron Pyrites.

Analyst	Pattinson.							Price & Nicholson.	Clapham.
Source	Spain.		Belgium.	Westphalia.	Norway.	Ireland.	Coal brasses.	Wales.	Cornwall.
Iron . .	38·70	41·41	39·68	38·22	39·22	40·52	31·44	49·72	32·20
Sulphur . .	44·60	49·30	45·01	45·60	45·50	44·20	38·10		34·34
Copper . .	3·80	5·81	. .	. .	1·80	0·90	trace	. .	0·80
Lead . .	0·58	0·66	0·37	0·64	. .	1·50	. .	. .	0·40
Zinc . .	0·30	trace	1·80	6·00	1·18	3·51	. .	. .	1·32
Thallium .	trace	trace	trace	trace					
Ferrous oxide .	. .	. .	.	. .	. .	. .	. .	11·01	
Lime . .	0·14	0·14	0·25	0·11	2·10	0·24	4·96	7·95	
Magnesia .	trace	trace	. .	. .	0·01	. .	0·33	5·74	
Carbonic acid .	. .	. .	. .	. .	1·65	. .	5·11	19·29	
Arsenic . .	0·26	0·31	trace	trace	. .	0·33	trace	. .	0·91
Oxygen . .	0·23	0·25	0·42	0·37	0·45	0·25	0·31		
Coaly substance	. .	. .	. .	. .	. .	. .	14·45	6·10	
Gangue . .	11·10	2·00	12·23	8·70	9·08	8·80	1·40	. .	29·0
Moisture . .	0·17	0·05	0·25	0·36	0·17	0·90	0·90		
	99·88	99·93	99·91	100·30	100·16	100·34	100·30	99·81	98·98

2. *White iron pyrites* (*Strahlkies*; *pyrene*), is a variety of iron pyrites of a white colour; it is also of frequent occurrence.

3. *Magnetic pyrites* (*Magnetkies; pyrite magnetique*), has a bronze colour with metallic lustre, and is slightly magnetic. Specific gravity 4·5 to 4·7. It occurs both crystalline or granular, and compact. In its purest state it contains 60·49 per cent. iron, and 39·51 per cent. sulphur.

4. *Arsenical pyrites* (*Mispickel; Arsenkies; fer arsenical*), has a steel grey colour, and metallic lustre. Specific gravity 6 to 6·2. It occurs in the same states as iron pyrites, frequently associated with tin ores, and contains 34·35 per cent. iron, 10·96 per cent. sulphur, and 56·79 arsenic. This mineral frequently contains a considerable amount of silver. Both it and the other varieties of iron pyrites sometimes contain gold, and varying proportions of other metallic sulphides, especially copper pyrites, with which they are frequently associated.

The residue left after separating sulphur from iron pyrites by roasting, is smelted to extract the copper it contains; and attempts are being made to use it also for obtaining the iron from it.

Of other native compounds of iron that occur in large quantities, the most important are the *chromate* (see CHROME IRON ORE, i. 939); the *titanates iserine*, and *ilmenite* (see TITANATES); the *tungstate* (see WOLFRAM); the *silicates* (see GREEN EARTH, ii. 944, and SILICATES); the *ferrous* and *ferric phosphates*. (See PHOSPHATES.)

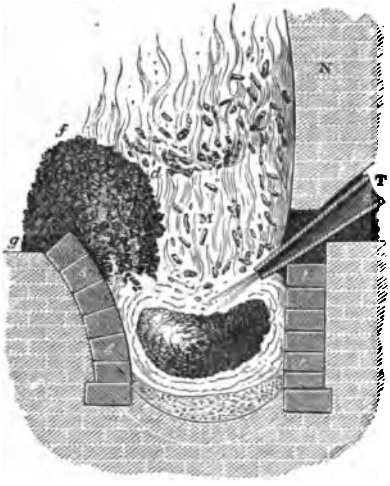
Preparation.—1. Pure iron may be obtained by heating pure ferric oxide in a current of hydrogen gas. If the reduction be effected at the lowest possible temperature, the iron is obtained in the state of a grey powder which is pyrophoric, and takes fire on contact with atmospheric air, being converted into ferric oxide. At a strong red heat the metal is obtained in a spongy state and is less readily oxidised.

2. A mixture of iron wire or iron filings, with one-fourth part of magnetic oxide, placed in a closely covered crucible, under a layer of powdered glass, free from heavy metallic oxides, and exposed to a white heat in a smith's forge, yields a button of iron containing only mere traces of carbon or other impurities.

Manufacture on the large scale.—Malleable iron may be obtained directly from iron ores by heating them with charcoal under the influence of a blast of air. Formerly, malleable iron was obtained by this method exclusively, but it is now practised almost only in Sardinia, the Pyrenees, India, some parts of America, Africa, and other countries where metallurgic art is less advanced than in the great iron-producing districts of Europe.

1. *Production of malleable iron direct from the ore.*—This is chiefly practised according to what is termed the Catalan method. It consists in heating the roasted ore with a charcoal fire urged by a blast, and in a manner very similar in its general character, to that adopted in working a smith's forge. The most important of the several arrangements for this operation, comprised collectively under the term "bloomery" (*Luppenfeuer*, *forge Catalan*), is the *hearth* (*Heerd; creuset*), which is a nearly cubical chamber built of stone, and lined with blocks of iron, *s*, *s*, *t*, *t*, at the back and front. It is placed against a wall N, N, through which the tuyere, T, of the blowing machine projects, as shown in *fig.* 573. The ore to be reduced is broken to pieces the size of a nut, and is placed against the front of the hearth, *s*, *s*, while the remaining space M, between it and the back *t*, *t*, is filled with charcoal, and when the hearth is filled in this way, the upper part of the heap of ore forms a ridge at *d*, *f*, *g*, the surface *f g*, being covered with a layer of closely packed charcoal dust (*brasque*). The fire is then urged by the blast and the ore becomes gradually deoxidised, while the gangue or earthy substance contained in the ore, combines with a portion of ferrous oxide, forming a fusible siliceous slag which collects at the bottom of the hearth. Fresh charcoal, and the finely divided ore, are constantly supplied to the fire meanwhile, and eventually the deoxidised mineral sinks down, in the state of malleable iron, to the bottom of the hearth, where a workman kneads together the fragments into a spongy mass, which is taken out of the fire, and rendered solid by hammering while still red-hot, so as to unite the metallic particles, and it is then drawn out into bars under a forge hammer.

Fig. 573.



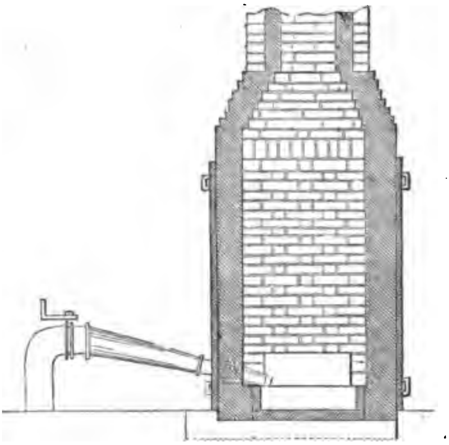
Only the richer kinds of ore can be treated in this way, and it always involves the waste of a large portion of the iron, which escapes reduction, and by entering into combination with the siliceous and earthy portions of the ore, forms a slag consisting chiefly of ferrous silicate. In the extraction of iron by this method, the reduction is effected, perhaps entirely, by carbonic oxide, and the carburation of the iron to such an extent as to determine the production of cast iron, is prevented by the want of an adequately high temperature.

2. *Indirect process.*—The production of malleable iron is now for the most part effected by operating upon cast iron so as to deprive it of the greater part of the carbon and silicon it contains, and at the same time to separate other admixtures that would be prejudicial to the quality of malleable iron. This operation is conducted in two ways, the one termed the charcoal finery, the other puddling. Both consist in a partial oxidisation of the cast iron, and production of a fusible ferrous silicate, which reacts upon the carburet of iron and determines the oxidation of the greater part of the carbon and other substances contained in the cast iron.

The main distinction between these two modes of operating is that, in the one case charcoal is employed in contact with the cast iron; while, in the other, coal is used in a reverberatory furnace, so that the iron is acted upon in a separate chamber without actual contact with the fuel, but only by the flame and heated gases produced by its combustion.

White cast iron containing a small amount of carbon is most suitable for conversion into malleable iron, because it does not melt so readily at a moderate heat and is not so liquid when melted as grey cast iron, but softens before melting and remains for some length of time in a viscous condition, which admits of its presenting a greater surface to the action of oxidising agents when stirred about. Its carbon is also more easily oxidised than the graphite of grey cast iron. When therefore grey cast iron has to be converted into malleable iron, it is in the first instance converted into white iron by a preliminary melting in the running-out fire (p. 349).

Fig. 574.

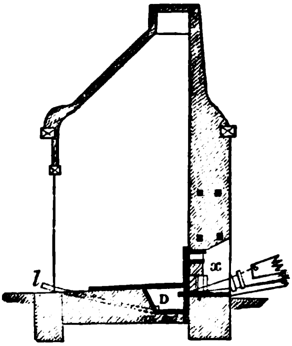


The production of malleable iron by the charcoal-finery, is practised in different places with a great number of minute variations, determined partly by the nature of the pig iron operated upon, partly by less important circumstances.

The charcoal-finery employed in Wales, and some other parts of the country, for manufacturing the sheet iron used for tin plates, which requires to be of very good quality, is represented in section by *fig.* 574. It consists of a quadrangular hearth lined with cast iron plates enclosed within brick walls and furnished with a blast apparatus. About 2 cwt. of pig iron, melted with coke in a similar kind of hearth, called a *melting finery*, is run into the hearth, covered with charcoal and stirred about, while the fire is urged by a blast of air until the iron becomes sufficiently decarburised to be malleable. Then it is collected in a *lump* (*Luppe; loupe*) at the end of an iron bar, and removed from the hearth for the purpose of being hammered into a prismatic slab about 2 inches thick. This is broken into pieces of about 25 lbs. each, called *stamps* (*schirbel; lopins*). About three of these stamps are piled upon the flattened end of an iron bar termed the *staff* or *portal*, and raised to a welding heat in a kind of reverberatory furnace termed the *hollow fire*, and again hammered into a slab about 3 inches thick, which is passed between rollers until it forms a sheet of the requisite thickness.

In Sweden the greater part of the best iron is made in a very similar manner, except that there, as well as in Germany and other parts of the Continent, the pig iron is melted in the same hearth in which it is converted into malleable iron. An ordinary form of the hearth employed is represented by *fig.* 575.

Fig. 575.



The pig iron is melted above the tuyere, so that it may not be exposed to the blast until it has become liquid, and the blast is regulated so as to retain the metal on the hearth in a proper state of fusion; the blast is then stopped, the slag run off, the iron raised off the hearth, and placed on the top of a fresh supply of charcoal, after which it is again melted. When the decarburation has advanced far enough, which may be judged of by the consistence of the metal, it is again raised up, covered with charcoal, subjected to a strong welding heat to melt away the slag, and then hammered out to a short bar, which is cut into pieces that are again welded together, and drawn out into bars under a hammer.

In order to appreciate the chemical nature of the process that takes place in the charcoal-finery, it is necessary to consider the composition of the slags. They consist essentially of silica and ferrous oxide, but may be divided into two classes, viz. poor slag (*Rohschlacke*) and rich slag (*Gaarschlacke*).

The poor slag is formed during the first melting of the pig iron and the earlier stage of the operation. It consists essentially of ferrous silicate. It is very liquid and solidifies rapidly, is of a blackish-grey colour with metallic lustre, crystalline, frequently variegated, and sometimes porous. The crystals have the form of olivine or iron chrysolite, and the composition of the slag approximates to that of this mineral.

Analyses of poor Slags from the Charcoal-finery.

Source	. .	. .	. .	Magdesprüng
Analyst	Mitscherlich.	Rammelsberg.	Walchner.	Wiegand.
Ferric oxide . .	. .	2·25		
Ferrous oxide . .	67·24	63·51	62·04	57·3
Manganous oxide .	. .	. .	2·64	4·5
Magnesia . . .	0·65	. .	1·40	
Lime . . .	. .	. .	. .	2·8
Alumina . . .	. .	. .	. .	3·0
Potash . . .	. .	. .	0·28	
Silica . . .	31·16	34·38	32·34	32·4
	99·05	100·14	99·70	100·0
Ratio of oxygen in bases to oxygen in silica . .	·914	·822	·868	·907
Percentage of iron .	52·30	50·69	48·25	44·95

The rich slag is formed during the latter stage of the operation. It is less liquid, and solidifies less quickly than the poor slag. It forms an agglutinated mass; is heavier, of a grey colour, and has a compact fracture. Its composition varies much, and the amount of iron is greatest in that formed at the end of the operation.

In the charcoal-finery process, the separation of the carbon, silicon, phosphorus, and manganese from pig iron is effected by the oxidation of these substances, partly by the blast and partly by the ferrous oxide contained in the slag, formed at the end of the operation.

Cast iron melted with ferric oxide yields carbonic oxide and iron. Iron containing silicon, when heated with iron oxides, yields ferrous silicate. The ferrous silicate constituting poor slag is not reduced, either by pig iron or by carbon, at a red heat; it is only at a very high temperature that there is a reaction between the carbon and ferrous oxide, with elimination of iron. The more highly basic ferrous silicates, constituting rich slag, on the contrary, are decomposed, even at a red heat, by pig iron, in such a manner that the excess of ferrous oxide is reduced, and a less basic ferrous silicate remains.

Analyses of rich Slag from the Charcoal-finery.

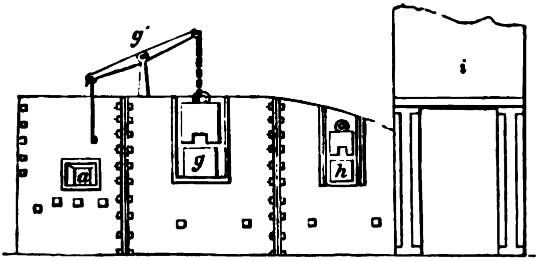
Name of works	Sweden.					Rybnik.	
	Gysinge.	Skebo.	Lauch-hammer.	Sauvigny.	Norway.	Silesia.	
Analyst . .	Winckler.	Sefström.	Lampadius	Berthier.	Ström.	Karsten.	Hoffmann.
Ferric oxide .	. .	. .	. .	. .	. .	. .	6·00
Ferrous oxide .	82·9	82·1	77·00	74·0	71·3	61·2	71·15
Manganous oxide .	. .	6·8	3·00	3·6	. .	6·7	
Magnesia . .	carbon and loss 3·2	2·8	. .	. .	2·7	2·4	0·46
Lime . . .		. .	1·75	1·8	. .	0·9	1·26
Alumina . .		. .	3·00	1·2	. .	0·2	
Potash . .							
Silica . . .	13·9	7·6	10·25	19·8	21·4	18·1	21·01
Phosphoric acid .	. .	. .	1·75	. .	3·7		
	100·0	99·3	99·75	100·4	99·1	99·5	99·88
Ratio of oxygen in bases to oxygen in silica . .	2·485	5·150	3·598	1·736	1·418	1·7	1·663
Percentage of iron	64·48	63·86	59·89	57·56	55·46	47·6	59·50

During the first stage of the process, the silicon of the iron, together with the oxidised iron, and any sand that may be present, contribute to the formation of poor slag; but as the oxidation of the iron continues, the slag gradually becomes richer in iron, and serves to a great extent as the medium by which the action of atmospheric oxygen upon the pig iron is exercised. Phosphoric acid and manganese also pass into the slag. The conversion of pig iron in this way must not be carried on too rapidly, especially in the case of the less pure varieties, or the oxidation of the silicon, phosphorus, &c., and their consequent separation, will not be fully effected; nor must it be too much protracted, or there would be unnecessary waste of iron by oxidation.

Hot blast has been employed in the charcoal-finery; but since the object of that operation is not so much to obtain a high temperature as to separate all the impurities of the pig iron, the blast cannot be so much heated as in other cases.

3. *Puddling; Frischen im Flammöfen; affinage à la houille.*—This is at the present time by far the most important method of manufacturing malleable iron, especially in this country. The main difference between the operation of puddling and that of refining with charcoal, consists in the use of a reverberatory furnace for the purpose, in order that the decarburation of the iron may be effected in a chamber separated by a wall or bridge from the fire-place where the fuel is burnt. The metal is thus kept entirely out of contact with the fuel by which the furnace is heated, and it is acted upon only by the flame and hot gas passing over the bridge into the working chamber. This arrangement admits of the use of mineral fuel in place of charcoal, and is requisite for the sake of preventing the iron from becoming contaminated with the impurities always present in mineral fuel in far larger amount than in wood charcoal.

Fig. 576.



The construction of the puddling furnace is represented by *fig.* 576 in elevation, and by *figs.* 577 and 578 in vertical and horizontal sections. It is built of brick, and cased with strong plates of cast iron, held together by iron bars. The fireplace is shown in the sections at *b b*, and the firing hole at *a* in the elevation; *c* is the bridge separating the fireplace from the working chamber *f*; *d d* the bed or hearth upon which the cast iron is melted and decarburised. This is now constructed of cast-iron plates covered with a layer of red iron ore, or some material containing abundance of ferric oxide. The working door *g* has a small hole at the bottom, through which the workman stirs about the metal in the furnace. Just below this door, level with the surface of the hearth, is a small hole called the floss or tap-hole, that can be closed with a plug, and through which the slag is run out from the hearth. Sometimes the slag is allowed to run away from a hole *k* below the chimney. The door *h* is for introducing a fresh charge of pig iron. The chimney *i* is generally from 30 to 50 feet high, and is furnished at the top with a damper for regulating the draught, as shown in *fig.* 579.

Fig. 577.

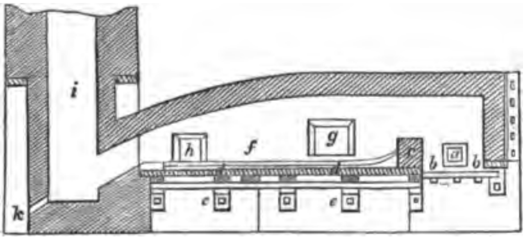
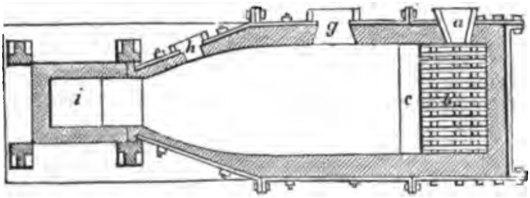
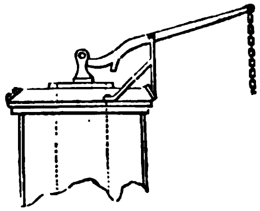


Fig. 578.



The pig iron to be decarburised is piled up on the hearth of the working chamber, and when, after a few minutes, it begins to melt, about 25 per cent. of hammer- or mill-scale is added. The metal is then broken up and stirred about with an iron bar called a rabble, worked through the small hole in the door *g*. This is continued until the whole mass is reduced to a kind of sandy, half-melted condition. The heat is then increased, and soon after the whole of the metal is melted, it begins to swell and heave as if boiling, while jets of blue flame issue from all parts of the mass. This is due to the formation of carbonic oxide by the reaction of the carbon in the metal with the ferruginous oxides present. As this reaction progresses, the iron becomes pasty, and in consequence of the oxidation of the silicon contained in the iron, and the formation of ferrous silicate, a liquid slag separates from it, and collects round the metal on the hearth, or flows away towards the floss *k*. When the separation of carbon from the metal has advanced to some considerable extent, the oxidising action of the atmosphere in the working chamber is lessened by lowering the damper and keeping the iron surrounded by highly carbonaceous or smoky gas. When the iron has become so far decarburised as to be malleable, or as it is termed "come to nature," it is gathered together and worked into several lumps with an iron bar, ready to be removed from the furnace.

Fig. 579.



A modified form of this operation is adopted at some works, under the name of "pig-boiling." The furnace used for this purpose is constructed much in the same way as the puddling furnace, except that for "pig-boiling" the hearth is much deeper and more pan-shaped than in the puddling furnace. The hearth is also covered with a thick layer of red iron ore, or roasted slag from the puddling furnace, and the decarburation of the pig iron is in this case effected probably more by the action of oxidised compounds of iron than by the direct action of atmospheric oxygen.

For detailed descriptions and drawings of the furnaces and machinery used in the manufacture of iron, see Truran, *Iron Manufactures of Great Britain*, London, 1862.

The presence of sulphur or of some metals, such as zinc, lead, and copper in the pig iron, retards the conversion into malleable iron, and in the case of pig iron that becomes very liquid when melted, is more difficult to bring it into a plastic condition than when it has the viscid character which good white cast iron, containing a small amount of carbon and a little sulphur, presents when melted. In puddling sulphury iron, there may be a very large waste, due to oxidation of the metal, in consequence of the greater time occupied in performing the last stage of the operation. It is the opinion of some that the presence of a certain amount of phosphorus in sulphury iron facilitates its working into balls.

The reactions that take place in puddling are essentially the same as those which take place in the charcoal refinery. Under the influence of the free oxygen in the atmosphere of the working chamber, a portion of the iron is oxidised, and at the same time the manganese, silicon, carbon, sulphur, and phosphorus present in the iron, are also oxidised, either by the direct action of air, or through the medium of the metallic oxides added to the pig iron, or formed during the process, the result being the production of a slag or cinder, consisting of ferrous and manganous silicates, and magnetic oxide, and containing the other earthy impurities present in the iron operated upon, as well as part of the sulphur and phosphorus, the one probably in state of sulphide, the other as phosphate. This will be evident from the following analyses of these slags.

Analyses of Slag from the Puddling Furnace, "Tap Cinder."

Works	Chillington.	Dowlais.			Broomsgrove.	Bromford.	Wales.
Analyst		Riley.			Percy.		Noad.
Ferric oxide .	16·42	13·53	8·27	17·00	23·75	17·11	
Ferrous oxide .	60·14	57·67	66·32	58·67	39·83	48·43	70·48
Manganous oxide	2·29	0·78	1·29	0·57	6·17	1·13	12·80
Alumina . .	trace	1·88	1·63	2·84	0·91	1·28	
Lime . .	0·70	4·70	3·91	2·88	0·28	0·47	
Magnesia . .	0·42	0·26	0·34	0·29	0·24	0·35	
Silica . .	15·30	8·32	7·71	11·76	23·86	29·60	8·24
Iron sulphide .	. .	7·07	. .	3·11	0·62	1·61	
Sulphur . .	traces	. .	1·78	. .	. .	. .	0·53
Phosphoric acid	4·66	7·29	8·07	4·27	6·42	1·34	7·66
Copper . .	. .	trace	trace				
	99·93	101·50	99·32	101·39	102·08	101·32	99·71
Percentage of iron	58·26	58·04	57·37	47·61	47·60	44·22	54·81

The elimination of sulphur and phosphorus from pig iron appears to be always attended with oxidation of the iron in a degree proportionate to the quantity of those substances separated from the metal. Consequently, in order that the waste of metal thus incurred in producing malleable iron of good quality may not exceed such a limit as would be tolerable in practice, it is essential that the amount of those substances in the pig iron operated upon should not be large. The smaller the amount of sulphur and phosphorus in the pig iron, the easier is its conversion into good malleable iron, and so far as the separation of those substances is concerned, the smaller is the waste experienced in this operation.

The manganese present in pig iron appears to be always separated almost entirely in the manufacture of malleable iron. The presence of manganese in pig iron appears to exercise, in some way not fully understood, a beneficial influence upon the quality of the malleable iron made from it by the operation of puddling. Experiments recently made by Caron (Compt. rend. xlvi. 828) appear to show that sulphur may be separated from pig iron by the influence of manganese during the decarbonisation, but that phosphorus is not separable in the same way. He operated upon iron containing 1·15 per cent. of sulphur. By melting it three times without any admixture, the amount of sulphur was reduced to 0·96 per cent; but by adding to it 6 per cent. metallic manganese, and by melting three times with access of air, the amount of sulphur was reduced to 0·8 per cent. The same iron melted with 10 per cent. ferric oxide showed a reduction in the amount of sulphur from 1·15 to 1·08 per cent., and by melting it with 10 per cent. ferric oxide and 6 per cent. manganese, the sulphur was reduced to 0·07 per cent.

The separation of silicon from pig iron in puddling, as in other modes of producing malleable iron, takes place very readily under the influence of oxidising conditions, with formation of ferrous silicate; and the chief importance attaching to its presence in pig iron employed for that purpose, relates more to the amount of malleable iron obtainable than to any special difficulty in the elimination of silicon. In the ferrous silicate constituting the slag of the puddling furnace, there is three and a half times as much iron as silicon; so that, if both the silica and the oxide of iron it contains originate from the oxidation of the pig iron operated upon, the waste of iron will be very considerable when the amount of silicon in the pig iron is large. Under the supposition that the slag is derived wholly from the metal by oxidation, the puddling of pig iron containing 5 per cent. of silicon would be attended with a waste of 15 per cent. of iron due to this cause alone, independently of that resulting from the separation of carbon, silicon, and other substances. Hence it is very desirable that the amount of silicon in pig iron intended for conversion into malleable iron should not be large.

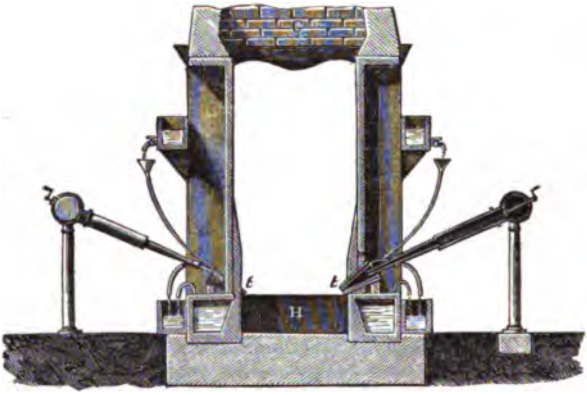
In that modification of the method of producing malleable iron known as "boiling," the pig iron does not undergo any preliminary treatment, and the furnace is sometimes charged with the liquid metal run direct from the smelting furnace, so as to save the fuel requisite for remelting it. But in puddling, the practice is generally to submit the pig iron beforehand to an operation known as *refining* (*Feinen; mazéage*), which consists in melting the pig iron, in contact with coke and with the aid of an air-blast, in a hearth similar to a charcoal finery, but larger, and termed a *refinery* or *running-out fire* (*Feinheerd; feu de finerie*). This operation, which, in fact, corresponds to the first melting of the pig iron under the blast in the charcoal-finery, has the effect of partially decarbonising the iron, and of removing from it the greater part of the silicon. At the same time grey pig iron is brought into the condition of white cast iron, which is most suitable for conversion into malleable iron by puddling. This change is facilitated by suddenly cooling the metal with water as it runs from the hearth. The composition of refined iron, or, as it is technically termed "*metal*" (*Feinesen; fine-metal*), and the change that takes place in the process, are shown by the analyses below.

Analyses of Refined Iron.

Works .	**Bromford.**	**Königshütte.**		**Ebbw Vale, Wales.**		**France.**	
Analyst .	**Dick.**	**Abel.**		**Noad.**		**Regnault.**	
		pig iron.	*refined.*	*pig iron.*	*refined.*	*pig iron.*	*refined.*
Iron . .	95·14	. .	. .	. .	. .	97·8	92·3
Carbon . .	3·07	. .	. .	. .	0·30	1·7	3·0
				2·40			
Silicon . .	0·63	4·66	0·62	2·68	0·32	0·5	4·5
Sulphur .	0·16	0·04	0·30	0·22	0·18		
Phosphorus .	0·73	0·56	0·50	0·13	0·09	. .	0·2
Manganese .	trace	. .	. .	0·86	0·24		
	100·17	100·00	100·00	100·00	100·00	100·00	100·00

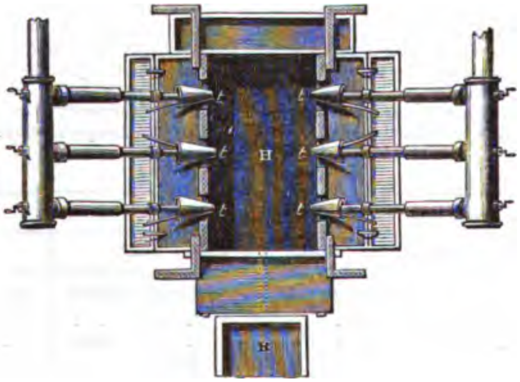
The refinery or running-out fire, represented by *fig.* 580, consists of a rectangular hearth H about 2 feet deep, and rather longer than it is wide. It is lined with cast-iron plates constructed so as to admit of being cooled by water circulating through them, and has three blast tuyeres *t*, *t* supplying hot air on each side. The chimney C is supported upon iron columns, and the spaces between them are closed with cast-iron plates. (See Truran, *op. cit.*, p. 193, *et seq.*)

Fig. 580.



A quantity of coke is put into the hearth, and after the fire has been sufficiently raised, about one or two tons of pig iron is placed on the top, covered with coke, and the fire urged by the blast until the whole of the metal has melted and run down into the hearth, where, under the oxidising influence of the blast, the carbon and silicon it contains are oxidised, and a slag is formed which floats on the surface of the metal. Fresh coke is added, meanwhile, and the heat kept up until the action has advanced sufficiently far. A hole level with the bottom of the hearth is then opened, and the melted metal run into a cast-iron mould B cooled externally by water; and a quantity of water is thrown upon it in order to cool it suddenly and to render the slag discharged from the hearth with it, more easily separable. Sometimes the charge of iron is run into the refinery direct from the blast furnace, and in some cases a quantity of hammer-scale or the slag from previous operations, is added to the charge, in order to facilitate the process of purification by which the silicon and other impurities are separated.

Fig. 581.



The slag produced in the operation of refining is vitreous, dark-coloured, black or bluish. It consists essentially of ferrous silicate, and generally contains the greater part of the manganese, as well as some of the phosphorus and sulphur that were present in the pig iron operated upon, together with the ash of the coke used as fuel.

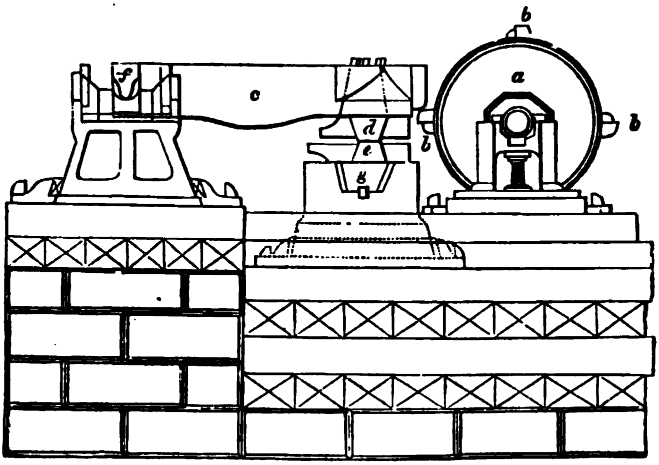
Analyses of Refinery Slag.

Name of works	Stourbridge.	Dowlais.		Bromford.
Analyst	Rammelsberg.	Riley.		Forbes.
Ferric oxide	13·09			
Ferrous oxide	73·22	65·52	54·94	61·28
Manganous oxide	. .	1·57	2·71	3·58
Alumina	. .	3·60	5·75	7·30
Lime	. .	0·45	1·19	3·41
Magnesia	. .	1·28	0·50	0·76
Silica	13·69	25·77	33·33	22·76
Sulphur	. .	0·23	. .	0·46
Iron sulphide	. .	. .	0·17	
Phosphorus	. .	1·37	0·99	
Copper	. .	. .	trace	
	100·00	99·79	99·68	99·55
Percentage of iron	66·11	50·96	42·84	47·66

The quantity of slag produced in puddling depends very much on the kind of pig iron operated upon, and also upon whether it has been previously refined or not. Grey iron and unrefined pig, containing the most considerable amount of silicon, afford a more abundant and more liquid slag than refined metal, the slag from which is proportionately richer in ferrous oxide, and being consequently less fusible, accumulates in a thick layer on the bottom of the hearth. It may also contain ferric oxide, in consequence of partial oxidation of the ferrous silicate, or of the ferrous oxide produced in excess of that requisite to form the silicate.

The lumps of decarburised iron obtained as above described are termed *puddle-balls* (*Bällen ; boules*), and consist of coherent spongy masses of malleable iron, intermixed with oxide and slag. In order to separate these admixtures and reduce the iron to a compact and uniform mass, the puddle-balls are removed from the working chamber of the puddling furnace while still at a welding heat, and either hammered or squeezed. This operation is termed "shingling" or blooming.

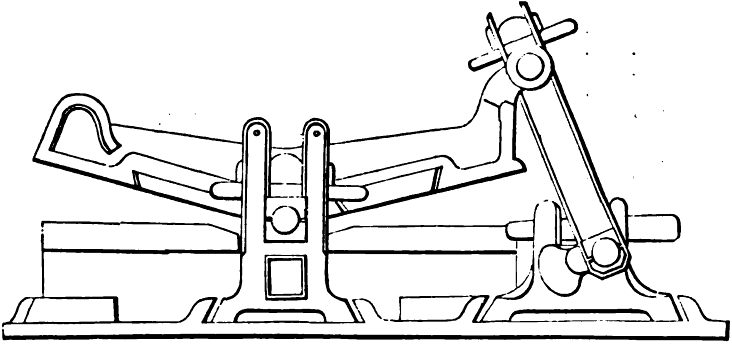
Fig. 582.



The hammers employed for this purpose, termed *forge hammers* (*Stirnhammer ; marteau frontal*), are very powerful, and are either constructed of cast iron as shown at *fig.* 582, or are steam hammers. In the former a massive beam *c*, 8 or 10 feet long, resting at one end on a fulcrum *f*, and having at the other end a ⊣ shaped head *d*, is lifted by the wipers *b*, *b*, *b* of the cam-wheel *a*, and, as that revolves, the hammer is let fall, at the rate of 70 or 80 strokes a minute, upon the anvil *e*, where the puddle-ball is placed. The *steam-hammer* (*Dampfhammer; marteau pilon*), consists of a block of iron, weighing several tons, attached to the piston of a steam-engine fixed above it, by which it may be lifted vertically in guides fitted to the frame work, and let fall upon the ball placed on an anvil.

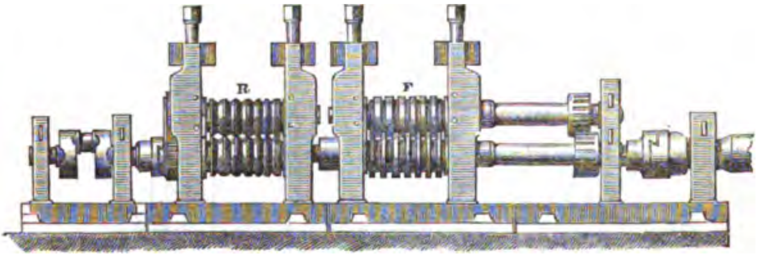
The machines employed for compressing puddle-balls are of various forms, and are termed *squeezers* (*Quetscher; presse à charnière*). One of the most usual kinds, represented by *fig.* 583, consists of a lever, worked upon a fulcrum at the centre, by a crank connected to one end, so that the jaws are alternately brought, at a rate of some 60 strokes a minute, nearer to the corresponding anvil-faces where the puddle-balls are placed to receive the pressure.

Fig. 583.



The puddle-ball, after having been hammered or squeezed, which occupies only a few seconds for each, is termed a *bloom* (*Luppe; loupe*), and is then drawn out into a bar by being rapidly passed several times, and while still red-hot, between grooved rollers, constituting what is termed a *forge-train* (*Streck-walzwerk, train de laminoir*), *fig.* 584. This consists of two pairs of rollers, R F, fitted in frames and driven by machinery. In one pair of rollers, called the *roughing rolls* (*Cannelur-Walzen; cylindres dégrossisseurs*), there are corresponding V-shaped grooves round the surface. In the other pair of rollers, termed the *finishing rolls* (*cylindres finisseurs*), the grooves are flat, and in both they gradually decrease in size from one end of the rollers to the other, so that by passing the blooms successively through several pairs of grooves, they are reduced to bars of from 7 to 3 inches wide by from 1½ to ½ an inch thick. In this condition the iron is termed "puddle bar," or No. 1 iron.

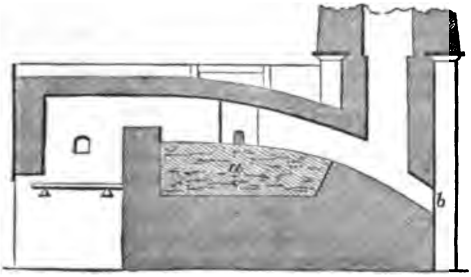
Fig. 584.



After leaving the rolls, these bars, while still hot, are cut into short lengths by shears, and the pieces tied together by strong wire in a bundle is termed a *pile* (*Paket; trousse*), which is brought to a welding heat in a reverberatory furnace called the "re-heating or mill furnace" (*Schweiss-ofen; four de chaufferie*), constructed somewhat like a puddling furnace, as shown by *fig.* 585. The hearth *a* of this furnace, on which the iron is placed, is made of sand, and slopes down towards the flue, so that any slag that is formed may run down and escape at the hole *b*, leaving the hearth quite dry.

The piles are raised as rapidly as possible to a full welding heat in the mill furnace, and are then removed with tongs to mill-rolls, of a similar kind to those already described, but more highly finished, and drawn into bars which are again cut up, piled, and then submitted to the same operations of heating and rolling several times, according to the required quality of the iron. Sometimes, after the first rolling of the iron into puddle bars, hammering is substituted in the place of drawing out between rollers. It is in this series of operations that the iron acquires its texture, and that close, uniform, and continuous fibre, upon which its strength and general good quality is considered to be chiefly dependent. The mode in which the pieces of iron are arranged in the piles is considered to be of great importance as regards the result obtained; but notwithstanding the strong opinions expressed on this subject, little is known as to the rationale of the connection apparently existing between the quality of the iron and the mode in which it is wrought.

Fig. 585.



A certain proportion of slag is produced during the reheating of the piles in the mill-furnace, which has a composition very similar to that of the slag from the puddling furnace, but the silica it contains is derived mainly from the sand forming the hearth.

Analyses of Mill-furnace Slag.

Works .	Dowlais.	Wasseralfingen.	Sweden.	
Analyst .	Riley.	Rammelsberg.	Dugendt.	Noad.
Ferric oxide . . .	. .	8·49	. .	5·00
Ferrous oxide . .	66·01	55·36	65·83	52·20
Manganous oxide . .	0·19	. .	0·74	
Alumina	2·47	. .	. .	9·60
Lime	0·81	0·36		
Magnesia	0·27	trace		
Silica	28·71	34·00	33·47	32·00
Sulphur	0·11			
Iron sulphide . . .	. .	. .	. .	1·95
Phosphoric acid . .	1·22	. .	. .	0·25
Copper	trace			
	99 79	98·21	100·04	100·00
Percentage of iron .	51·34	49·0	51·20	45·34

When all these successive operations have been completed, the iron is in the condition known as "merchant iron," and the different degrees of quality are indicated as No. 2, No. 3, &c., or as "common," "best" and "best best," as well as by particular brands.

Besides the waste of iron resulting from the formation of slag in refining, puddling, &c., there is always a further waste due to the oxidation of the iron during the shingling, hammering and rolling to which it is subjected. The product of this oxidation consists chiefly of magnetic oxide, which forms a crust on the surface of the hot iron, and falls off in scales, constituting what is known as "hammer-scale" or *mill-scale* (*Hammerschlag; battitures de fer*).

The total waste of iron in the conversion of pig iron into malleable iron, varies according to the kind of pig iron operated upon, and the amount of impurities in it, as well as upon the skill of the workmen. In South Staffordshire, the waste amounts to from 18 to 22 per cent. on the pig iron. In South Wales it sometimes amounts to from 26 to 28·5 per cent., though it is sometimes less than 13 per cent. Formerly the waste amounted in some cases to from 34 to 35 per cent. (Truran, *op. cit.* p. 215). The introduction of iron bottoms for puddling furnaces, in place of sand, has contributed largely to reduce the waste of iron due to the formation of slag, and the use of materials containing ferrous or ferric oxides, as admixtures in the puddling or boiling operation, in all probability tends to compensate the waste that would result from atmospheric oxidation, inasmuch as the oxidation effected by these admixtures would be accompanied by an equivalent elimination of metal from them.

The greater part of this waste of iron takes place in the refining, amounting on the average to about 10 per cent. on the pig iron. In puddling refined metal, the waste is not more than from 4 to 7 per cent. In the mill-furnace the waste is much less, varying, according to the number of reheatings, and the size to which the iron is rolled, from 3·5 to 10 per cent. The consumption of iron in any stage of the manufacture, requisite to produce a ton of iron in a subsequent stage, is technically called the "yield," by a somewhat singular inversion of the meaning of the term.

The consumption of fuel in the various stages of the conversion of pig iron into malleable iron, varies according to the skill of the workmen, as well as the kind of fuel and iron used. In refining, from 6½ to 8 cwt. of coke per ton of metal made, is used when the pig iron has to be melted, and from 4 to 5 cwt. when the melted metal is run in from the blast furnace direct.

In "pig-boiling," the consumption of coal varies from 18 to 22 cwt. per ton of bar iron made, according as the coal is more or less bituminous and capable of burning with flame.

In puddling refined metal, the consumption is about 10 to 14 cwt. of bituminous coal, and from 17 to 18 cwt. of anthracitic coal per ton of iron made.

In heating the piles, the consumption of fuel is from 7 cwt. to 13 cwt. per ton of merchant bars, according as they are larger or smaller.

In connection with the consumption of fuel in the conversion of pig iron into malleable iron, it will be interesting to consider what amount of the heat, capable of being generated by the coal consumed, is really effective; how much of it is really used in heating the iron.

The temperature to which the iron requires to be heated in the puddling furnace may be taken as expressed by 1650° C.; and, assuming that the specific heat of cast iron increases above 350° C. in the same ratio that it does up to that temperature, it would, in that case, be about 0·26 at 1650° C.; accordingly, the quantity of heat requisite to raise iron from 15° C. to that temperature would be:

heat units.

$$424{\cdot}84 = 1650 - 15 \times 0{\cdot}26.$$

A further quantity of heat would be consumed in melting the iron, and though the latent heat of iron has not been determined, it may be assumed as equal to 30 heat units. Thus the total heat requisite to heat cast iron up to 1650° C. and to melt it would be:

heat units.

$$454{\cdot}84 = 424{\cdot}84 + 30.$$

and the quantity of heat requisite for one ton of iron would be:

heat units.

$$1{,}018{,}841{\cdot}6 = 2240 \times 454{\cdot}84.$$

Taking the average calorific power of coal, expressed in heat units, to be 7,778, it appears from the foregoing calculation, that the quantity of heat actually communicated to the iron amounts to less than that capable of being generated by 131 pounds of coal. Thus:

Coal, lbs.		Calorific power, heat units.		Quantity of heat generated, heat units.	Quantity of heat required to heat 1 ton of iron from 15° to 1650°C. and to melt it, heat units.
131	×	7,778	=	1,018,918	1,018,841·6.

Then, taking the quantity of coal consumed in puddling as being equal in weight to the pig iron worked, it appears that only 133 pounds out of every ton of coal burnt in the puddling furnace is really effective in heating the iron, or not more than one-sixteenth part. But though the quantity of heat actually communicated to the iron bears only this small proportion to the whole quantity generated by the combustion of the fuel used, it must be remembered that, under existing circumstances, this large consumption of fuel is unavoidable, since it is indispensable that, during the whole of the operation, the temperature should be maintained sufficiently high to keep the iron melted. For this purpose the rate of combustion must be high, and the intensely heated products of combustion must pass rapidly through the working chamber of the furnace. It has been estimated that in the ordinary puddling furnace, when the consumption of coal is at the rate of 240 pounds per hour, the volume of heated gas passing through the working chamber amounts to upwards of 72 cubic feet per second, or sufficient to fill the working chamber twice in a second, and that this is necessary in order to counteract the influence of conduction and radiation in reducing the temperature. (See Prideaux, *Elementary treatise on Fuel, particularly with reference to Reverberatory Furnaces.*)

It is in consequence of the extremely high temperature required to be maintained in puddling and mill furnaces, that only so small a fraction of the heat generated by combustion of the fuel consumed, is really effective in heating the iron (FUEL, ii. 729), inasmuch as it is only the heat corresponding to the difference existing at any moment between the temperature of the iron, and the higher temperature of the atmosphere in the working chamber of the furnace, that is available for maintaining or raising the temperature of the iron. So long therefore as the temperature of iron in a puddling furnace requires to be 1650° C., the gas passing into the chimney must be at a temperature not less than that, and the whole of the heat corresponding to the quantity of gas discharged at that temperature into the chimney, will be without any other useful effect. A variety of arrangements have been contrived for turning this waste heat to account in raising steam for driving the machinery of iron works; and by far the most simple and convenient plan consists in doing away with the separate chimney to each furnace, and conducting the heated gas escaping from the working chamber of several puddling furnaces, into a spacious underground culvert, extending some distance away from the furnaces, and communicating with flues passing through and round a large Cornish boiler, along which the gas passes, and, after communicating its heat to the water, is then discharged into a lofty chimney capable of producing a draught sufficient for all the furnaces connected with it.

A great number of attempts have been made to introduce other improvements in the method of producing malleable iron by puddling; such, for instance, as the use of a blast of hot air, or of steam, or a mixed blast of air and steam, rotary puddling furnaces, &c., but excepting the admixture with the pig iron of materials containing ferruginous oxides, and the use of iron hearth-bottoms in the puddling furnace, none of these projects appear to have either any such scientific basis as to appear promising, or to have been attended with sufficient success to demand consideration.

The case is different as regards the application of gaseous fuel in the refinery, puddling furnace, and mill furnace. The gas used for this purpose is either the combustible gas evolved from the throat of the blast furnaces in which pig iron is made, or it is made specially from small coal and other inferior kinds of fuel, by burning them in such a manner that the carbonic acid generated by the combustion of one portion, is made to pass through a mass of incandescent fuel, so as to be converted into carbonic oxide, which, together with the hydrocarbon vapours driven off from the fuel, passes into the furnace to be heated, and is there burnt, much in the same manner as coal gas is burnt in a Bunsen's burner (See Bischof: *Die indirecte aber höchste Nutzung der rohen Brennmaterialen*, 1848; also Scheerer, *Metallurgie*, i. 339). This method of using fuel has long been practised in Germany, and is now being introduced at some of the iron works in this country, where it is to be hoped it will eventually not only admit of coal being used in iron working, without those disadvantages arising from the presence of sulphur and other impurities, when it is in contact with the metal; but that it may likewise become an important means of economising fuel, and especially of turning to good account the vast quantities of small coal that have hitherto been almost entirely wasted. For descriptions of gas generators, and gas refining, puddling, &c., see the works above quoted, and Percy, *Metallurgy*, ii. 596, 674, 716; *Ure's Dictionary of Arts, Manufactures, &c.* ii. 573.

4. *Atmospheric process.*—Under this designation, an entirely new method of producing malleable iron from pig iron, has been proposed within the last few years as a substitute for the operation of puddling. It consists in submitting melted pig iron to the action of a current of air forced through it until it is sufficiently decarburised. The heat generated during this process, by the combustion of the carbon and silicon, and some portion of the iron, is sufficient to heat the metal above the melting point of malleable iron, so that, when the operation is ended, the decarburised iron is obtained in a liquid condition, and may be run into ingots, which are afterwards to be forged into bars. (Bessemer, specifications, 1855, Nos. 2321, 2768; 1856, Nos. 356, 630.)

The main principle of this method is to effect the conversion of pig iron into malleable iron, wholly by the direct influence of atmospheric oxygen, and independently of that reaction between the pig iron and the ferruginous or manganese oxides, or materials containing them, which takes place in the operation of puddling or boiling, and which, according to all experience, and to such scientific data as there are for forming an opinion, is so important a condition of the separation of sulphur and phosphorus from pig iron. The result of the trial of this new method of producing malleable iron affords a still further confirmation of the important influence of the reaction referred to as taking place in puddling. By the new method pig iron may be wholly decarburised, and the silicon it contains may be entirely eliminated with ease; but the case is very different as regards the sulphur and phosphorus: for these substances, which are so detrimental to malleable iron, far from being separated from the pig iron subjected to this new mode of treatment, are either wholly unacted upon, or so little affected, that, relatively, they are augmented, the amount of phosphorus in the decarburised iron obtained by this method, being greater than it was in the pig iron operated upon, while the amount of sulphur is but little reduced, as will be seen by the following analyses:

	Pig iron, per cent.	Bessemer iron, per cent.
Analyst .	Tookey.	
Carbon	3·309	0·218
Silicon	0·595	
Sulphur	0·485	0·402
Phosphorus	1·012	1·102

At the present time no means of obviating this defect are known; consequently, the application of this method is confined to the working of such kinds of pig iron as are practically free from sulphur and phosphorus; and hence, as regards the greater part of the malleable iron manufactured in this country, there is no possibility of the adoption of this method, although it admits of the decarburation of pig iron with much greater ease, and much more rapidly than the operation of puddling. In Sweden, on the contrary, where the pig iron produced is far less contaminated with sulphur and phosphorus than most of that made in this country, the new method is being worked with great advantage. In England, it is also being applied in working some of the better and more costly kinds of pig iron, but chiefly for the purpose of producing a kind of steel which bears a higher price than ordinary malleable iron. For this reason the further consideration of this method will be included in the article on Steel.

5. **Iron smelting.**—In the extraction of iron from such of its ores as are suitable for metallurgic purposes, and as it is now chiefly practised in iron-producing countries, the metal is always obtained in the carburetted state, commonly known as cast iron, pig iron, or crude iron. The processes comprised in the smelting of iron are:—

1. The separation of water, carbonic acid, sulphur, and other volatilisable substances from the ore by the action of heat.
2. The reduction of the iron from the state of oxide, as it exists in the ore, to the metallic state, by the action of carbonic oxide.
3. The separation of the earthy substances, commonly present in iron ores, from the reduced metal, in consequence of the formation, at a high temperature, of fusible compounds of those substances; and
4. The carburation and melting of the reduced metal.

In smelting the richer kinds of iron ore, *calcination* or *roasting* (*Röstung; grillage*) is not always requisite for the removal of volatilisable substances; but with the majority of the iron ores used in that operation, it is very desirable that they should undergo this preparatory treatment, as will be seen by reference to the analyses of iron ores; and in all cases calcination is advantageous, inasmuch as it has the effect of rendering the ore more porous, and consequently more susceptible of being reduced.

The calcination of iron ores is effected by heating them to dull redness in contact with air, either in heaps, with layers of coal at the bottom and alternating with layers of the ore; or in kilns built of brick or masonry, from which the roasted ore can be drawn out at the bottom. The careful regulation of the heat applied is the most important requisite in the calcination of iron ores, and it should be only just sufficient to expel the volatilisable substances, without effecting, in the case of carbonaceous ores, the reduction of iron to the metallic state, or, in the case of siliceous ores, the formation of ferrous silicate and fusion of any portion of the ore, so as to render it more compact.

The changes effected by calcination consist chiefly in the separation of water, carbonic acid, and bituminous substance when the ores are carbonaceous. In this case there may be a partial deoxidation of the ore, attended with formation of ferrous or magnetic oxide; but more generally the calcination of iron ores has the effect of producing ferric oxide to a greater or less extent, if the iron is not already in that state.

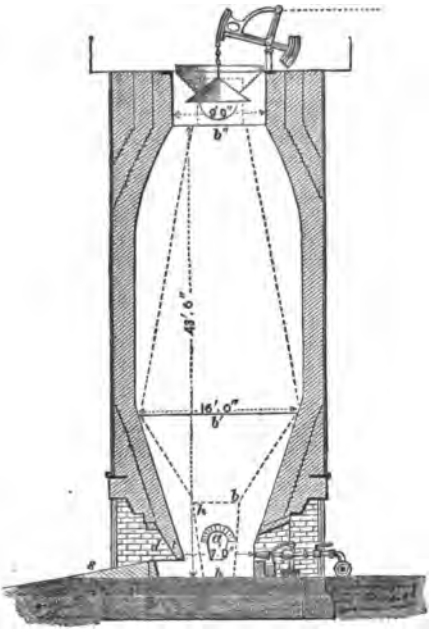
The sulphur in iron ores, generally present in the state of pyrites, is also to a great extent separated from them by calcination, in consequence of the decomposition of the pyrites; one half of the sulphur being volatilised, while the residual iron sulphide is converted by oxidation into sulphate, which may be decomposed if the heat is sufficiently great. The entire separation of sulphur from iron ores in this way is seldom practicable.

An alteration of some kinds of iron ore similar to that resulting from calcination, especially as regards separation of sulphur, is effected by exposing them for a time to the atmosphere. In this process of *weathering* (*Verwitterung*), pyritic minerals are oxidised and converted into sulphates, which may be washed out to some extent by rain, and this change, together with the peroxidation of the ore that takes place in some cases by contact with atmospheric air, has the effect of disintegrating the ore and rendering it more porous.

Sometimes the separation of the volatilisable constituents of iron ores, instead of being effected by a preliminary operation, takes place in the blast furnace, and is then the first stage of the process of smelting, the heat requisite for the purpose being derived from the current of gas ascending through the charge. It is probable that in some cases this plan may be attended with economy of fuel, and that if the height of the shaft could be increased, so that the upper part would serve as a substitute for the calcining kiln, the temperature of the gas discharged from the throat might be reduced to a minimum, and the whole of the heat generated in the furnace thus rendered effective. But there is a practical limit to the adoption of this plan, consisting in the friable character of some kinds of fuel and ore, and their liability to become crushed by the weight of a high column of materials in the shaft. In the Cleveland district, where the ore is used in large masses, and the fuel used is a very hard coke, furnaces have been built with this object 75 feet high, and the temperature of the gas has been reduced on the average to about 258° C. instead of 381° C. (I. L. Bell, *Industrial Resources of the Tyne, Wear, and Tees*, p. 107). But this saving is only partial, and since the calcination of ores in the blast furnace is attended with disadvantages as regards other modes of applying the waste heat of the gas discharged from blast furnaces (see p. 354), it yet remains to be seen whether that plan can be adopted so as to realise the greatest possible degree of economy in fuel.

The smelting of iron ores is conducted in a furnace consisting essentially of two parts, viz., the hearth, which is a circular chamber, built of stone and lined with fire-brick, where the combustion of the fuel and the melting of the reduced ore and flux take place, and the shaft, which is a wider cylindrical chamber, built above the hearth, and continuous with it, where the charge of ore, flux, and fuel continuously supplied at the top, is subjected to the action of the heated gas resulting from combustion, before reaching the hearth. The precise form and dimensions of this furnace, which is termed a *blast furnace* (*Hohofen; haut fourneau*) vary considerably (see Truran, *op. cit.* pp. 22, 124, *et seq.; Percy, *Metallurgy*, ii. 350, 475, and 559). One of the most approved forms is represented by *fig.* 586. In this case, the distinction between the hearth, *a' a'*, and the shaft, *b b' b''*, is less marked than it is in some furnaces where the hearth is not more than two or three feet wide, with its sides vertical and terminating in a decided angle at the junction with the lower part of the shaft, *b b'*, termed the *boshes* (*Rast; étalage*), which in the older form of furnaces, was more inclined than in the figure, while the *shaft* (*Schacht; cuve*), *b' b''*, was much more conical, and formed a decided angle at its junction with the upper part of the boshes, or widest part of the furnace, termed the *belly* (*Kohlensack; ventre*), so that the interior sectional contour corresponded to the dotted outline shown in the figure. In the furnaces of this form, the upper portion of the hearth is termed on the Continent the *Gestell; ouvrage*, and the lower portion, where the melted materials collect, the *Crucible* (*Heerd; creuset*).

Fig. 586.



At one side of the hearth, there is an opening formed by an arch, *t*, called the *tymp* (*Tümpel; tympe*), and below this arch the hearth is prolonged outwards somewhat beyond the plane of the tymp, as far as the block of stone *d*, called the *dam* (*Wallstein; dame*), over which the melted slag flows away to the "cinder fall," *s*, through a depression called the *cinder notch* (*Schlackentrift*), in the upper surface of the dam. Through the bottom of one side of the dam, there is a channel, called the *tapping hole* (*Stichloch; trou de coulée*) communicating with the hearth, to admit of the melted metal collected at the bottom of the hearth being run out at intervals. This channel is stopped up with clay or sand, while the metal and slag are accumulating in the hearth. That side of the furnace towards which the hearth is prolonged, is called the *front* (*Arbeitsseite; partie antérieure*), while the opposite side is called the *back* (*Rückseite; partie postérieure*). At this side there is an arched opening, *a*, called the *tuyere hole* (*Form*) and there is generally a similar opening at each of the other sides. Opposite each of these openings an arch is turned in the outer brickwork of the furnace to admit of access to the tuyere holes. The upper extremity of the shaft is called the *throat* (*Gicht; guelard*), and is generally surmounted by a low wall or chimney, called the *tunnel head*, with openings at the side for introducing the materials into the furnace.

Air is supplied to the furnace through a series of pipes connected with a blowing engine, each pipe terminating with a conical tube called a *tuyere* (*Duse; tuyère*), surrounded with a hollow conical sheath, through which passes a stream of water to prevent the melting of the tuyeres, extending through each of the tuyere holes as far as the interior surface of the hearth.

In the working of a blast furnace, the shaft is kept nearly filled with the solid materials used; these are introduced at intervals into the upper end, and gradually sink down as the smelting progresses. Meanwhile a continuous supply of air is forced into the lower end of the furnace through the tuyeres, under a pressure of from $\frac{1}{2}$ to 2 lbs. per square inch in charcoal furnaces; and from 2 to 5 lbs. per square inch in furnaces worked with coal or coke, and in quantity proportionate to the size of the furnace and its rate of working, so as to maintain a rapid combustion of the fuel at that part of the furnace immediately above the level of the tuyeres. (See Truran, *op. cit.*, p. 115.)

The reduction of the ferruginous oxides in the ore is effected by the reaction taking place at a high temperature between these oxides and carbonic oxide, produced by the combination of carbonic acid, resulting from combustion of the fuel, with a further quantity of carbon equal to that it contains; and, since ferric oxide contains 30 per cent. of oxygen, the carbon and air requisite in these reactions for the reduction of a quantity of ferric oxide containing 1 pt. of iron will amount to:

Iron.		Ferric oxide.		Parts by weight of carbon requisite in the state of carbonic oxide.		Parts by weight of oxygen requisite to form carbonic acid with half the carbon.		Air.
1	=	1·429	=	0·3214	=	0·4285	=	1·863

or somewhat about 8 cwt. of coal, containing 80 per cent carbon, and 1 ton 17 cwt. 29 lbs. of air, or 54,443 cubic feet, per ton of iron made.

The reduction of the ferruginous oxide in the ore is not alone sufficient for the production of the metal in an available condition: for it is but seldom that iron ores do not contain a considerable admixture of earthy substances which require to be separated. They generally consist chiefly of silica, clay, or carbonate of lime, as will be seen by reference to the tabulated analyses of iron ores. These substances being intimately mixed with the ferruginous oxide, and consequently with the reduced metal, it is necessary that they should be melted as well as the metal itself, in order that they may separate according to their different densities in the liquid state. Any one of these substances alone is infusible at the temperature commonly produced in iron smelting, and they can be separated only by being converted into sufficiently fusible compounds. The double silicates containing two or more bases, are substances whose fusibility corresponds to the requirements of this case, and it is by the formation of such a vitreous silicate, termed *slag* (*Schlacke; laitier*), capable of being readily melted, that the separation of the earthy admixtures in iron ores is effected.

It is but rarely that these admixtures are of such a nature, and present in such relative proportions, as to produce, under the influence of heat, a silicate that would be suitable for the purposes of iron smelting. Hence it is necessary to mix with the ore some substance that will effect this result. The nature and proportion of this *flux* (*Zuschlag; castine*) will of course depend upon the composition of the ore to be smelted, and must be regulated in accordance with the general principles relating to the production of slags. (See Metallurgy.)

In smelting iron ores in which the earthy admixture is chiefly calcareous, clay or some siliceous material, such as forge cinder or the roasted slag from puddling furnaces, is added as a flux, or the ore may be mixed, in suitable proportions, with ores containing silica or clay. In the more frequent case of ores containing clay, or silica in some form, the material used as a flux is limestone or quicklime, in order to effect the formation of a double silicate containing alumina and lime as its basic constituents.

The fusibility of the double lime and alumina silicates varies according to the proportion existing between the silica and the bases, as well as that between the two bases. The most fusible of them are those in which the oxygen of both bases amounts to two-thirds of that in the silica, and the oxygen of the lime equals that in the alumina.

In smelting iron ores with charcoal, the temperature of the furnace is generally lower than when they are smelted with coke or coal, and on that account the slag requires to be more fusible than in the latter case. In smelting iron ores with coke or coal, especially when hot blast is used, the temperature is so much higher than in furnaces worked with charcoal—not only where fusion takes place, but also at the upper part of the furnace—that the slag requires to be rendered less fusible by increasing the proportion of lime to such an extent, in relation to the silica and alumina in the ore, that fusion may not take place before the reduction of the ore has been completely effected, and that the fragments of the charge may not become agglutinated, but remain loose and porous while passing through that portion of the shaft where reduction takes place, and consequently more capable of being permeated by the reducing gas.

In the smelting of siliceous ores there is a further necessity for the addition of lime, even more important than that connected with the production of a suitably fusible slag. This arises from the circumstance that the double silicate, containing alumina and ferrous oxide as its basic constituents, is very fusible, and from the consequent tendency to the formation of this compound, the result of which would be that a considerable amount of the iron would escape reduction to the metallic state, and pass off in the slag, thus giving rise to considerable loss of iron, besides other serious inconveniences. This combination of ferrous oxide with the aluminous silicate in the ore does not take place in the presence of a sufficient amount of lime, and in order to prevent it as much as possible, the quantity of lime added to the ore is generally such as to form a slag in which the oxygen of the bases is equal to that in the silica.

Analyses of Slags from Blast Furnaces.

Locality	Edsken, Sweden.	Peitz.	Königshütte.		Rübeland, Hartz.	Hammhütte.	Siegen.	Olsberg, Westphalia.
Ore used	—	Bog iron ore.						Red and brown iron ore.
Fuel used	Charcoal.							
Kind of iron made					Mottled pig.		Specular iron. Hot blast.	
Analyst	Ullgren.	Karsten.						Rammelsberg.
Ferrous oxide	0·95	1·45	0·2	. .	2·44	21·5	0·06	1·27
Manganous oxide	1·86	1·40	11·6	4·30	2·20	29·2	33·96	3·16
Alumina	4·30	6·25	6·7	12·60	13·04	2·1	6·63	5·71
Lime	38·64	19·71	26·9	42·85	25·67	. .	. .	27·60
Magnesia	7·40	0·70	. .	. .	0·57	8·6	10·22	7·01
Potash	0·30							
Soda	1·38							
Silica	46·37	70·12	54·1	39·60	53·79	37·8	48·39	55·25
Phosphoric acid	traces							
Sulphur	0·03	0·37	0·5	0·65	. .	0·80		
	100·00	100·00	100·00	100·00	97·71	100·00	99·29	100·00
Ratio of oxygen in bases to oxygen in silica	0·697	0·257	0·480	0·917	0·512	0·547	0·572	0·385
Ratio of oxygen in bases to oxygen in alumina	7·301	2·180	3·293	2· 00	1·400	15·000	3·730	3·037
Percentage of iron	0·740	1·130	0·160	. .	1·900	16·720	. .	0·990

Analyses of Slags from Blast Furnaces—continued.

Locality	Mägdesprung, Hartz.				Eisenerz, Styria.	Sweden. Gesberg.	Sweden. Gesberg.	Sweden. Edsbra.
Ore used	Spathic, red, and brown iron ore.				Magnetic iron ore.			
Fuel used	Charcoal.							
Kind of iron made	Hot blast.							
Analyst	Rammelsberg.			Bromeis	Wehrle.	Oengren	Sjögeen.	Follin.
Ferrous oxide	4·03	0·44	3·25	5·83	1·4	1·68	3·29	1·0
Manganous oxide	25·04	24·85	24·53	22·18	28·6	2·81	2·63	4·1
Alumina	5·88	4·96	11·27	5·12	2·6	6·62	5·38	5·1
Lime	20·56	26·66	21·55	20·00	10·4	19·35	19·81	18·0
Magnesia	2·41	1·10	0·82	2·18	1·3	10·46	7·12	13·3
Silica	39·99	41·49	38·58	43·58	54·6	58·60	61·06	58·1
Sulphur	. .	. .	. .	CaS 1·11	1·1			
	97·91	99·50	100·00	100·00	100·0	99·52	99·29	99·6
Ratio of oxygen in bases to oxygen in silica	0·752	. .	. .	. .	0·458	. .	. .	0·451
Ratio of oxygen in bases to oxygen in alumina	0·481	. .	. .	. .	8·951	. .	. .	4·825
Percentage of iron	3·130	0·340	2·420	4·560	1·090	1·310	2·460	0·780

Analyses of Slags from Blast Furnaces—continued.

Works	Dowlais.			Dudley.	Russell's Hall.	Providence, Charleroi, Belgium.	Russell's Hall.	Cwm, Celyn.
Ore used	Clay iron ores of the coal measures.							
Fuel used				coke.	coke.			
Kind of iron made	white forge pig.		grey pig.	hot blast.				white pig
Analyst	Riley.			Percy.	Forbes.	Percy.	Dick.	Noad.
Ferrous oxide	3·08	6·91	0·76	1·27	0·93	4·94	1·00	19·80
Manganous oxide	1·02	1·67	1·62	0·40	2·79	2·26	2·20	1·53
Alumina	11·55	15·51	15·13	14·11	13·01	13·05	12·91	20·20
Lime	32·09	23·81	32 82	35·70	31·43	32·53	29·92	10·19
Magnesia	3·78	4·38	7·44	7·61	7·27	1·06	4·79	2·90
Potash	1·53	1·98	1·92	1·85	2·60	2·69	0·87	1·10
Silica	45·23	44·88	38·48	38·05	37·91	42·06	47·08	42·96
Phosphoric acid	. .	0·43	0·15	. .	. .	0·19	0·05	
Calcium	1·04	0·59	1·23	0·82	3·65	1·03	1·78	1·32
Sulphur	0·83	0·47	0·99					
	100·15	100·63	100·54	99·81	99·56	99·81	100·60	100·00
Ratio of oxygen in bases to oxygen in silica	0·716	0·691	0·99	1·01	0·953	0·81	0·691	0·822
Ratio of oxygen in bases to oxygen in alumina	2·18	1·45	1·85	2·09	2·15	1·88	1·87	0·929
Percentage of iron	2·39	5·37	0·60	0·99	0·62	3·84	0·80	15·40

The characters that are generally considered to be indicative of the formation of a suitable slag, consist in its being sufficiently liquid to separate perfectly from the metal, though as it flows from the furnace it is generally somewhat viscous. When solidified, it should not be vesicular, but compact and homogenous, without being either very vitreous or stony. The colour of slag from blast furnaces varies very much, but does not afford much indication of its character. When charcoal is used as fuel, the slag is lighter coloured than that from furnaces in which coal or coke is used.

The published analyses of blast furnace slags are very numerous; but comparatively few have any real value, from the absence, in most instances, of any statements as to the conditions under which the slags were produced. For the elucidation of the processes that take place in the smelting of iron ores, so far as the formation of slag is concerned, it is essential that the analyses of slags should not only be numerous, but that they should also be accompanied by descriptions of the kind of iron made, and the working condition of the furnace, as well as of the kind of ore, fluxes, and fuel employed. The analyses on pp. 359 and 360 will serve to illustrate the general character of the slag produced in iron smelting.

In some kinds of iron ore, the relation existing between the silica and alumina is very different from that generally obtaining in the clay iron ores of the coal measures, as will be seen from the following table and by reference to the analyses of ores.

	Low Moor.	Brierly.	Stanton.	Butterley.	Parkgate.	Cleveland.
Alumina . .	23	24	20	26	24	25
Lime . .	9	9	13	11	13	27
Magnesia . .	8	7	17	9	19	14
Silica . .	60	60	50	54	44	34
	100	100	100	100	100	100

In consequence of this difference, and the greater proportion of alumina in the ores of the Cleveland district, the slags produced in smelting them are much more stony and less vitreous than those produced in smelting other ores. An increased addition of lime would not remove this difference, which is due to the deficiency of silica in proportion to the alumina present, and is probably accompanied by a less degree of fusibility of the slags. This circumstance will perhaps serve to account for the apparent necessity of a very high temperature in the smelting of these ores, and for the failure of the attempts that have been made to smelt them with cold blast. (I. L. Bell, *loc. cit.* p. 95.)

Analyses of Slags from Cleveland Ores.

Name of works	Clarence, Middlesbro'.				
Ore used . .	Clay iron ore smelted with coke and hot blast.				Flue dust from blast furnace gas.
Analyst . .	Crowder.	Clarence Laboratory.			
Ferric oxide	. .	. .	. .	. .	8·20
Ferrous oxide	0·72	3·64	0·61	0·32	
Manganous oxide . . .	0·35	1·02	trace	0·80	
Zinc oxide	. .	. .	. .	. .	4·60
Alumina	24·69	20·72	22·28	21·70	16·00
Lime	40·00	36·88	40·45	38·72	12·15
Magnesia	3·55	4·25	7·21	6·10	0·57
Potash	0·46	0·50	. .	. .	0·40
Soda	0·99	. .	. .	. .	6·85
Silica	27·65	30·40	27·80	29·92	34·82
Phosphorus	0·26	. .	. .	0·07	
Sulphur	1·95	1·34	2·00	1·61	8·80
Chlorine	. .	. .	. .	. .	1·56
Water	. .	. .	. .	. .	5·60
	100·62	98·75	100·35	99·24	99·55
Ratio of oxygen in bases to oxygen in silica	1·675	2·042	1·687	1·600	
Ratio of oxygen in bases to oxygen in alumina . . .	1·127	2·394	1·392	1·346	
Percentage of Iron . . .	0·560	2·830	0·470	0·250	

The preceding analyses of slags from furnaces in which the Cleveland ores are worked, will illustrate the difference between them and the slags produced in other districts.

The precise mode in which the carburation of iron takes place in the blast furnace is not known. From the fact that iron becomes carburated when heated in contact with hydrocarbon gases, or even with carbonic oxide, and since these conditions obtain in the blast furnace, it is highly probable that carburation may take place before the reduced iron reaches that part where there is a temperature high enough for fusion.

The state in which the carbon exists in the iron obtained from the blast furnace appears to depend very materially upon the temperature at which fusion takes place. The lower the temperature, the greater is the proportion of the carbon combined with the iron, and any circumstance which tends to induce fusion at a low temperature is almost invariably attended with the production of white iron. This is the case when charcoal is used as fuel, when the ore is readily fusible, and also when it is highly refractory and has not a suitable admixture of flux to determine fusion. When a furnace is worked with a large amount of ore in proportion to the fuel, or, as it is termed, with a "heavy burden," and when sulphur is present to any large extent, there is from the same reason a tendency to the production of white iron.

The production of grey iron containing carbon in the graphitic condition appears to require a temperature far beyond that of mere fusion, and it is probable, on that account, the introduction of carbon in this form may be due to action more of a physical than chemical nature, and consist in solution of the carbon by the melted metal rather than actual combination. When sulphur is present in any of the materials used in smelting iron, it is necessary to employ a very high temperature in order to obtain grey iron, because the melting point of iron is considerably lower when it contains sulphur.

Besides the reduction of the ferruginous oxide in the ore and the separation of its earthy constituents by the formation of a suitable silicate, it is necessary to maintain a very high temperature at the lower part of the furnace for the fusion of these products. This is effected by the rapid combustion of fuel under the influence of a blast of air forced in through the tuyeres.

The kind of fuel employed in smelting iron ores has a great influence both on the quality of the iron produced and on the mode of working. With bulky porous fuel, such as charcoal, combustion takes place more readily than with the more compact and denser kinds of mineral fuel, and from the greater liability of charcoal to crumble under pressure, the furnaces in which it is used are generally much smaller than those worked with coal or coke. But the main difference between these two kinds of fuel, as regards the smelting of iron, consists in the relative freedom of charcoal from earthy substances, and its entire freedom from sulphur and phosphorus, which are so prejudicial to the quality of iron. Hence the greater purity of the iron smelted with charcoal, provided the ore used be free from deleterious admixtures.

The consumption of fuel requisite in smelting iron for the production of a sufficiently high temperature of fusion, far exceeds the amount requisite for the reduction and carburation of the metal, which, as already pointed out, is less than half the weight of the iron produced, whereas that consumed for melting may amount to from one to two or three tons per ton of pig iron made.

The consumption of fuel in iron smelting is one of the most important points with regard to the economical production of the metal, and it is exceedingly desirable to reduce it to the lowest possible limit. The amount of fuel consumed per ton of pig iron made varies considerably, not only according to the kind of fuel, its calorific power, combustibility, texture, etc., but also according to numerous other circumstances. Among these the shape of the furnace has an influence, in so far as it admits of the easy and uniform descent of the charge in the shaft, and less fuel is consumed in making white iron than in making grey or foundry iron; but probably the most important difference in the consumption of fuel is that resulting from the use of air at the ordinary atmospheric temperature, or air previously heated to a temperature considerably higher.

In charcoal furnaces, the consumption per ton of pig iron made, is from half a ton to two tons and upwards, according as hot or cold blast is used. In smelting with coal or coke, the consumption is from two to three tons and upwards with cold blast, and from 23 cwt. to two tons with hot blast.

The fuel is introduced into the furnace at intervals alternately with the mixture of ore and flux, and in uniform proportions, termed the *charge* (*Beschickung; lit de fusion*), and the relative proportion of fuel or of ore is termed in either case the "yield;" sometimes also in the case of the ore it is termed the "burden."

The total weight of the charge per ton of pig iron made, will vary, according to the kind of ore, flux, and fuel used, from four to five or seven tons and upwards, when the materials are used in the raw state; but by far the greater quantity of the material supplied to a blast furnace in smelting iron, consists of the air by which combustion is supported: for taking carbonic oxide to be the ultimate though not the immediate product of the combustion, the quantity of air required would amount to at least five times the weight of the fuel burnt, taking the combustible portion of the fuel to be equal to 85 per cent. of carbon, and allowing for the carbon consumed in carburating the iron. Consequently the total quantity of air supplied to blast furnaces will be as follows, according to the consumption of fuel given above:

	tons. cwt.	tons.	tons.	
Fuel consumed . . .	23	2	3	per ton of iron made.
Quantity of air . . .	5 15	10	15	
Cubic feet at 60°F. . .	168,038	292,240	438,360	

The greater part of this air is consumed in burning that portion of the fuel exclusively concerned in the production of a temperature high enough for effecting fusion; and that part which is consumed in the combustion of the fuel requisite for the reduction of the ore, does not amount to quite twice the weight of the iron made.

The temperature of the gaseous products of combustion discharged from blast furnaces differs according to the kind of materials used and their condition, the height of the shaft, and the mode of working. In the case of charcoal furnaces, the gas has generally a temperature of from 300° to 400° C., while that from furnaces worked with coke or coal, is from 550° to 1000° C., according to circumstances. The whole of the heat corresponding to the temperature of the gas discharged is waste heat, and although it has served, at an earlier stage of the process, to produce the high temperature necessary for fusion of the metal and slag, it is still available for any purpose to which it can be applied.

The great extent to which the heat generated in the smelting of iron ores is thus dissipated, without producing the full useful effect of which it is capable, may be judged of from the fact that the weight of the gas discharged from a blast furnace is more than equal to the entire quantity of both air and fuel consumed, or from 8 to 17 tons per ton of pig iron made.

But besides the waste of heat due to the high temperature of the gas discharged, there is a further and more considerable loss of heat, due to the fact that it contains a large amount of carbonic oxide, together with some hydrocarbons and hydrogen, and is in all ordinary cases sufficiently combustible at the temperature at which it is discharged, to take fire on coming in contact with atmospheric air at the top of the furnace. This waste is proportionate to the extent to which carbonic oxide is produced. Taking the average consumption of fuel in iron smelting to be represented by a quantity of carbon equal to twice the weight of the pig iron produced, if that portion only which is requisite for the reduction of ferric oxide be ultimately discharged from the furnace in the state of carbonic acid, the quantity of fuel fully utilised in producing the entire heating effect of which it is capable, will be only about one-sixth part of the whole.

Quantity of heat generated
by perfect combustion
of carbon.
parts by weight
2 : 0·3214
Heat units . 16160 : 2596 = 6·225 : 1

Then, since the calorific power of carbon burnt to carbonic oxide is only about one-third of its calorific power when burnt to carbonic acid, or as

2473 : 8080 = 1 : 3·223,

the heating effect produced by the remaining five-sixths of the fuel consumed, so far as regards its ultimate condition when discharged from the furnace, will be less than one-third the effect it is capable of producing:

Quantity of heat capable of being generated by combustion of 1·6786 carbon to carbonic acid. heat units.		Quantity of heat generated by combustion of 1·6786 carbon to carbonic oxide. heat units.						Difference.
13564	—	4151·1778	=	1·6786	×	2473	=	9413

the difference representing the heating effect capable of being produced by the carbonic oxide, and amounting to no less than 58·25 per cent. of the whole heating effect capable of being produced by the fuel consumed.

So far, therefore, as regards the condition in which the products of combustion are discharged from a blast furnace, the only portion of the fuel consumed so as not to be further available as a source of heat, is that equivalent to the reduction of the iron in the ore, and, supposing the metal to be contained in the ore in the state of ferric oxide, it would be only about one-third the weight of the iron made, or 16 per cent.

of the fuel consumed. The greater part of the heat corresponding to the remaining 84 per cent. of fuel consumed, leaves the furnace in some form or other in the gas, as sensible heat, or as heat capable of being generated by combustion, and is still available for heating purposes.

But, notwithstanding this large difference between the amount of fuel fully utilised and that which still remains available as a source of heat, after its combustion in the blast furnace, it must not be supposed that the large amount of fuel consumed in iron smelting, as compared with the amount which is fully utilised, does not, in the blast furnace, exercise its full heating power. For though only a small portion of the whole heat generated is rendered latent by the fusion of the metal, &c., the whole of it is required for producing the temperature at which those changes take place; that part which passes off in the gas does not indicate a useless consumption of fuel, and can only be regarded as waste heat, in so far as it is allowed to escape without being turned to such further advantage as it is still capable of.

In the immediate neighbourhood of the tuyeres, the fuel is burnt, under the influence of the blast, to carbonic acid, generating the full amount of heat corresponding to its calorific power, and producing there the greatest increase of temperature it is capable of producing when burnt with atmospheric air. (See Fuel, ii. 726.)

It is at this part of the furnace that, while the fuel is being consumed, the reduced metal and the earthy substances mixed with it are rapidly melted, and, falling down into the hearth, make room for a fresh quantity of the materials in the shaft of the furnace to sink down and undergo the same change, while the gaseous products ascend and communicate their heat to the materials in the higher part of the shaft.

When the iron ore smelted contains carbonic acid or water, and has not been previously calcined, those substances will be separated during the descent of the charge in the shaft, and will mix with the products of combustion. This will also be the case with the carbonic acid of the limestone used as a flux, and if coal be used as fuel, its volatilisable portion will likewise be expelled, and mix with the ascending gas.

In proportion as the extent of this admixture is greater, the gas will have a lower heating power when burnt, and therefore it is desirable to reduce the amount of carbonic acid and water-vapour in the blast furnace gas, by previous calcination of the ore and limestone, whenever the gas is to be used as fuel.

As a consequence of the different physical conditions of the products resulting from the changes that take place in smelting iron ores, those products are continuously discharged from the blast furnace in a manner exactly the reverse of that in which the raw materials are supplied to it; the melted iron and slag flowing out at the bottom, while gas escapes from the top or throat of the furnace.

In considering more minutely the conditions under which these products are formed, and the chemical nature of the changes from which they result, it will be convenient to follow the course of the air supplied to the furnace as it passes from the bottom to the top.

The direct and perfect combustion of the fuel is, in all cases, confined within a comparatively small portion of the furnace, and in furnaces worked with charcoal, it extends only to a short distance above the level of the tuyeres. Beyond that portion of the furnace, heat is communicated to the materials in the upper part of the furnace by the ascending heated gaseous products of combustion, consisting of a mixture of nitrogen and carbonic acid, the temperature of the gas being proportionally reduced thereby as it passes up to the mouth of the furnace. But since the materials in that part of the furnace immediately above the region of combustion are at a high red heat, the carbonic acid enters into combination with a further quantity of carbon, and is converted perhaps entirely into carbonic oxide, its volume being thereby doubled. This reaction being attended with a considerable absorption of heat (see Fuel, ii. 727), the temperature of that part of the furnace where it takes place, though still very high, must be, on that account, much lower than it is within the region of direct combustion near the tuyeres.

The following analyses of gas, taken from different heights in the shafts of blast furnaces, will serve in some degree to illustrate the nature of the changes resulting from the reaction taking place between the solid and gaseous materials contained in the furnace, and *figs.* 587 and 588 represent the shape of two of the furnaces from which the gases were taken.

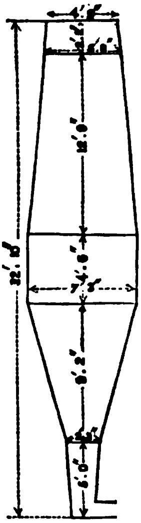
The formation of carbonic oxide is probably one of the most important features of this process: for there is every reason to consider that the reduction of the iron ore, as it descends towards the boshes of the furnace, is effected mainly, if not entirely, by this gas, aided perhaps in some cases, by hydrocarbon vapour or gas produced from the fuel by the action of heat. Previously to this, no alteration of the relative proportion existing by weight or volume, between nitrogen and oxygen in atmospheric air, would be effected either by the combustion of the fuel or by the subsequent

Analyses of Gas from Blast Furnaces.

Name of Works, &c.		Depth below the mouth.	Percentage composition by measure.							
		feet	Nitrogen.	Carbonic acid.	Carbonic oxide.	Marsh-gas.	Olefiant gas.	Hydrogen.	Cyanogen.	Ratio of oxygen to nitrogen.
ALFRETON, *Derbyshire.* Fuel: coal. Hot blast = 330° C. Bunsen and Playfair.	1	5	55·35	7·77	25·97	3·75	0·43	6·73	. .	0·374
	2	8	54·77	9·42	20·24	8·23	0·85	6·49	. .	0·375
	3	11	52·57	9·41	23·16	4·58	0·95	9·33	. .	0·418
	4	14	50·95	9·10	19·32	6·64	1·57	12·42	. .	0·368
	5	17	55·49	12·43	18·77	4·31	1·38	·62	. .	0·375
	6	20	60·46	10·82	19·48	4·40	. .	4·83	. .	0·340
	7	23	58·28	8·19	26·97	1·64	. .	4·92	. .	0·371
	8	24	56·75	10·08	25·19	2·33	. .	5·65	. .	0·381
	9	34	58·05	. .	37·43	. .	. .	3·18	1·34	0·322
SERAING, *Belgium.* Fuel: coke. Hot blast = 100° C.	10	1	57·06	11·39	28·61	0·20	. .	2·74	. .	0·450
	11		56·64	11·39	28·93	. .	. .	3·04		
	12	4	59·64	9·85	28·06	1·48	. .	0·97		
	13	9	62·46	1·54	33·88	1·43	. .	0·69		
	14	9⅝	61·67	1·08	35·20	0·33	. .	1·72	. .	0·301
	15		61·15	1·13	35·35	0·29	. .	2·08		
	16	11⅜	61·34	0·10	36·30	0·25	. .	2·01		
	17	45	54·63	. .	45·08	0·07	. .	0·25	. .	0·412
VECKERHAGEN, *Hesse Cassel.* Fuel: charcoal. Bunsen.	18	3	62·34	8·77	24·20	3·36	. .	1·33	. .	0·334
	19	4·5	62·25	11·14	22·24	3·10	. .	1·27		
	20	6	66·29	3·32	25·77	4·04	. .	0·58		
	21	7·6	62·47	3·44	30·08	2·24	. .	1·77	. .	0·295
	22	9	63·89	3·60	29·27	1·07	. .	2·17	. .	0·285
	23	12	61·45	7·57	26·99	3·84	. .	0·15		
	24	15	64·58	5·97	26·51	1·88	. .	1·06	. .	0·296
BAERUM, *Norway.* Fuel: charcoal. Ore: magnetic iron ore. Scheerer.	25	9	64·43	22·20	8·04	3·87	. .	1·46		
	26	12	62·65	18·21	15·33	1·28	. .	2·53	. .	0·413
	27	14	63·20	12·45	18·57	1·27	. .	4·51		
	28	17	64·28	4·27	29·17	1·23	. .	1·05	. .	0·293
	29	19	66·12	8·50	20·28	1·18	. .	3·29		
	30	22	64·97	5·69	26·38	. .	. .	2·96	. .	0·290
CLERVAL, *France.* Fuel: charcoal. Hot blast = 175°–190° C.	31	throat	57·79	12·88	23·51	. .	. .	5·82		
	32	3	57·80	13·96	22·24	. .	. .	6·00	. .	0·434
	33	8	58·15	13·76	22·65	. .	. .	5·44		
	34	12	59·14	8·86	28·18	. .	. .	3 82	. .	0·387
	35	16	60·54	2·23	33·64	. .	. .	3·59		
	36	17½	63·07	. .	35·01	. .	. .	1·92	. .	0·279
	37	tuyere	56·08	0·31	41·59	. .	. .	1·42		
CLERVAL. Fuel: charcoal. Cold blast. Ebelmen.	38	3¼	57·22	12·01	24·65	0·93	. .	5·19	. .	0·424
	39		58·56	11·95	23·85	1·33	. .	4·31		
	40	9⅝	60·92	4·14	31·56	0·34	. .	3·04	. .	0·327
	41		60·89	4·23	31·34	0·77	. .	2·77		
	42	19⅔	63·04	0·49	35·05	0·36	. .	1·06	. .	0·206
	43		63·06	0·07	35·47	0·31	. .	1·09		
	44	27⅝	61·22	. .	37·55	0·10	. .	1·13		
	45		58·17	0·93	39·86	0·25	. .	0·79	. .	0·359
AUDINCOURT, *France.* Fuel: charcoal. Hot blast = 250° C.	46	throat	55·62	12·59	25·24	. .	. .	6·25	. .	0·453
	47	11¼	54·39	14·46	23·62	. .	. .	7·53		
	48	14¾	56·07	9·55	28·82	. .	. .	5 56		
	49	18	57·84	7·54	30·03	. .	. .	4·59	. .	0 391
	50	21⅚	57·87	3·81	34·28	. .	. .	4·04		
	51	26⅙	61·61	0·21	36·39	. .	. .	1·79	. .	0·298
WRBNA, *Styria.* Fuel: charcoal. Hot blast = 200° C. Tunner.	52	11	70·50	16·39	13·11	. .	. .	. .	. .	0·325
	53	17	71·36	17·80	10·89					
	54	23	68·81	9·60	21·59	. .	. .	. .	. .	0·296
	55	27	66·66	2·68	30·66	. .	. .	. .	. .	0·270
	56	34	66·34	11·60	20·06	. .	. .	. .	. .	0·327

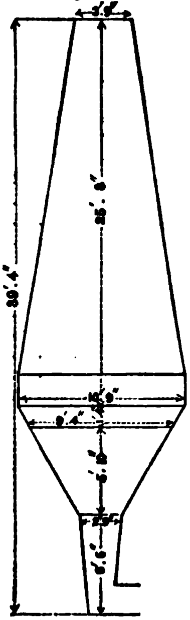
production of carbonic oxide. But by the reduction of the ore resulting from the reaction of carbonic oxide with ferrous or ferric oxides at a high temperature, carbonic acid is again produced, equal in volume to the carbonic oxide undergoing the change, and the effect of this transfer of oxygen from the solid to the gaseous contents of the furnace would be to produce a proportionate alteration of the ratios existing between both the relative weights and volumes of the nitrogen and oxygen. However, the influence exercised by this change on the composition of the gas passing upwards through the furnace will be slight; for, since the consumption of fuel in smelting iron ores so far exceeds the amount that would be chemically sufficient for the mere reduction of the ferric oxide, and since it is probable that the whole of the carbon consumed passes into the state of carbonic oxide at some part of the furnace not far above the level of the tuyeres, it follows that the extent to which carbonic acid is produced by the reaction between ferric oxide and carbonic oxide, must be small compared with the total amount of carbonic oxide produced in the operation; and, in fact, taking the consumption of fuel to be at the rate of 2 pounds carbon to 1 pound of pig iron made, only one-sixth part of the carbonic oxide formed at the lower part of the furnace, would be converted into carbonic acid by the reduction of the iron in the ore from the state of ferric oxide, taking place at the upper part of the furnace.

Fig. 587.



Norwegian charcoal blast furnace.

Fig. 588.



English blast furnace. Alfreton, Derbyshire.

Most probably the reduction of ferric oxide by carbonic oxide takes place progressively, and since the temperature requisite does not exceed that of dull ignition, it may extend over a considerable range in the descending column of materials, in proportion to the temperature prevailing in the upper part of the furnace.

From the relation existing between the calorific power of iron and that of carbonic oxide (see Heat, p. 105), it is probable that the reduction of ferric oxide by carbonic oxide, generates a certain amount of heat, since the quantity of heat generated by the combustion of iron is less than that generated by the combustion of the carbonic oxide requisite for its reduction from the state of ferric oxide. Thus:

Quantity of heat generated by combustion of 0·75 lb. carbonic oxide, heat units.		Quantity of heat generated by combustion of 1 lb. iron to ferric oxide, heat units.		Difference.
1802·25	−	1582	=	220

Unless, therefore, the thermal effect of the combustion of carbonic oxide by the condensed oxygen in ferric oxide, be different from that of its combustion by gaseous oxygen, this change would be attended with an increase of temperature. But in any case it does not appear that there is any other cause operative in reducing the temperature at the upper part of the blast furnace, save the transfer of heat from the ascending gas to the colder materials supplied from time to time at the top, as the charge descends, and—if hydrated or carbonated ores, or limestone, or fuel containing volatilisable substance, be used—the absorption of heat accompanying the change of water into vapour and of carbonic acid into gas.

Consequently, the maintenance of a high temperature in the upper parts of the blast furnace must have the effect of preparing the materials constituting the charge, for passing rapidly through that stage of the process taking place near the level of the tuyeres, which, as regards the present system of working, consists probably in the mere fusion of the metal and slag, and the combustion of the remaining fuel. Accordingly, a reduction in the quantity of material in the charge would admit of a given temperature being maintained at the upper part of the furnace with a less consumption of fuel; and since the time occupied in heating the materials in the furnace to such a temperature as will determine their fusion, is directly proportionate to the quantity of materials to be heated, and inversely proportionate to the temperature of the ascending gas, other conditions being equal, such a reduction would also admit of an increase in the rate of working or production of the blast furnace, and thus effect a saving of both time and fuel.

Then, since the consumption of fuel over and above that requisite for the reduction of the ore, and equivalent, as already shown, to about one-third the weight of iron produced, is incurred chiefly in order to effect the fusion of the charge, it follows that any mode of supplying the heat requisite for this purpose, otherwise than by the combustion of fuel in the furnace, would admit of a reduction in the amount of fuel supplied in the charge, and, what is still more important, a proportionate reduction in the supply of air. As a consequence of that twofold reduction, a smaller quantity of heat would suffice to bring the charge to a given temperature in a shorter time. The greater the substitution of the extraneous source of heat for the combustion of fuel in the furnace, the nearer would be the approximation of the amount of fuel requisite in the charge to that minimum limit which is necessary for the reduction of the ore, and the greater would be the utilisation, in the blast furnace, of the full calorific and reducing power of the fuel.

These considerations will serve to illustrate the principle of the economy, both in time and fuel, resulting from the use of hot blast in iron smelting. The apparently paradoxical result of a greater thermal effect being produced by a less consumption of fuel, has given rise to a vast deal of misconception in regard to this subject, and has even led to the entire denial of any advantage attending the use of hot blast.

In smelting iron ores with mineral fuel, which almost always contains sulphur, a portion of this substance is retained by the slag, probably in the state of calcium-sulphide; but the pig iron generally contains some sulphur, and it is desirable to reduce the amount to the smallest practicable limit. The means that are considered to be capable of effecting this object are, increasing the proportion of lime in the slag, and the addition of materials containing manganese, both of which appear to determine the separation of a larger portion of sulphur in the slag.

The amount of silicon in pig iron appears also to be influenced by the proportion of lime in the charge. At the high temperature obtained in smelting with hot blast, silica is reduced, in all probability, to a greater extent than is generally the case with cold blast, and the presence of an additional amount of lime may render that reduction more difficult; but the observations that have been made on this subject are not sufficiently decisive to show that this is really the case.

The pig iron obtained by smelting phosphatic ores almost invariably contains the greater part of the phosphorus in the ore. Experiments made on this subject by Messrs. Price and Nicholson (Phil. Mag. Dec. 1855) show that this is not due to the influence of hot blast, as had been supposed; but that it is the natural result of the easy reducibility of phosphoric acid. Their investigations also lead to the conclusion that the separation of phosphorus in the slag is closely connected with the partial reduction of the ore, and the presence of a large amount of ferrous oxide in the slag; and that the production of iron free from phosphorus from phosphatic ores, such as bog iron ore, involves a large waste of iron in this way, whereas by the perfect reduction of the ore, the whole or greater part of the phosphorus passes into the iron. As yet no means of preventing this result are known, and at the present time the elimination of phosphorus is probably one of the most important problems connected with the chemistry of iron smelting.

The investigation of this and similar subjects is, however, attended with very great difficulty. The nature of the operations by which iron is produced do not readily admit of being conducted experimentally; while on the other hand it is to a great extent essential that any investigation of the processes involved in those operations should be conducted on a large scale. Consequently, though numerous attempts have been made, both by iron smelters and chemists, to investigate the chemistry of this art, and though in many instances their labours have been well directed and to some extent fruitful, still the advance that has been made in knowledge of the subject is far less than what is needed; and without in the least detracting from the merit of some who have directed their attention to the subject, it may be said that, considering the national importance of this manufacture, as well as the magnitude of the interests concerned, the chemical contributions made during the last thirty years to its elucidation and improvement have been in the highest degree meagre, desultory, and unsatisfactory.

B. H. P.

IRON, ALLOYS OF. The alloys of iron are not for the most part of much importance. The softer metals, silver, zinc, tin, antimony, &c. acquire greater hardness, and sometimes greater tenacity, by taking up a few parts in a thousand of iron. True alloys of iron may be prepared by fusing different metals with iron wire, in a blast furnace, a small quantity of ferric oxide being added to decarbonise the iron.

1. An alloy of iron and aluminium, nearly in the proportion Al^2Fe, is obtained by melting 10 pts. aluminium and 5 pts. ferrous chloride with 20 pts. of a mixture of the chlorides of potassium and sodium in equivalent proportions, and treating the resulting crystalline regulus with dilute hydrochloric acid. The alloy then remains in iron-coloured six-sided prisms; it is attacked by hydrochloric acid, and soda-ley extracts from it a small quantity of aluminium (Michel, Ann. Ch. Pharm. cxv. 104). See also ALUMINIUM (i. 155). The peculiar excellence of the Indian steel, known under the name of "wootz," has been ascribed to the presence of aluminium in it; but there is room for doubting whether this is the case (Faraday and Stodart, Quart. Journ. of Science, 1819–20, ix. 320; Karsten, *Eisenhüttenkunde*, i. 484). (See STEEL.)

2. With Antimony (i. 316).

3. With Arsenic. *Arsenical Iron*, *Arsenosiderite*.—Two compounds of arsenic and iron, Fe^4As^3 and FeAs, known by these names, occur as natural minerals. They appear to be isomorphous, forming trimetric crystals, in which $\infty P : \infty P = 111° 30'$ (Greg), 122° (G. Rose); cleavage rather distinct in one direction; also massive. Hardness = 5—5·5. Specific gravity, from 6·80 to 8·71. Lustre metallic. Colour between silver-white and steel-grey. Streak greyish black. Fracture uneven. Brittle. Heated in a glass tube, they yield a sublimate of metallic arsenic; on charcoal before the blowpipe, they give off arsenical fumes and leave magnetic globules. Nitric acid dissolves them with separation of arsenious acid.

Arsenical iron always contains sulphur, generally between 1 and 2 per cent.; a specimen from Geier, in the Erzgebirge, contains 6 per cent. If this be reckoned as arsenical pyrites (mispickel), Fe^2AsS, the remainder is found to contain, in the lighter varieties (specific gravity 6·24—7·00), from 67·4 to 68·4 per cent. arsenic, and 32·6 to 31·6 iron, agreeing nearly with the formula Fe^4As^3, which requires 66·8 As and 33·2 Fe; and in the heavier varieties (specific gravity 6·80 to 8·71), from 71·35 to 73·49 arsenic, and 27·88 to 26·51 iron, agreeing nearly with the formula FeAs, which requires 72·84 As and 27·16 Fe. (*Rammelsberg's Mineralchemie*, p. 19.)

Arsenical iron occurs, associated with copper-nickel, at Schladming in Styria; with serpentine at Reichenstein in Silesia, and at Löling, near Hüttenberg, in Carinthia, in a bed of spathic iron ore, associated with bismuth and scorodite; at Geier in the Erzgebirge; in Bedford County, Pensylvania, and in Randolph County, North Carolina, where a mass was found, weighing nearly two pounds. (Dana, ii. 61.)

Gehlen, by melting 54 pts. iron with 108 pts. arsenic in a closed vessel, obtained an arsenide of iron, having nearly the composition Fe^2As; it was white, brittle, and very easily pulverised. Arsenical cast iron (see *ante*, p. 335).

4. With Bismuth.—An alloy prepared by melting together 3 pts. bismuth and 1 pt. iron is still magnetic.

5. With Copper. (See ii. 42.)

6. With Gold.—1 pt. iron forms with $\frac{1}{4}$ pt. gold a silver-white alloy; with 1 pt. gold, a grey alloy.

7. With Lead.—The two metals unite with difficulty when fused together, forming two alloys, arranged one above the other, the lower containing but very little iron, and the upper but a very small quantity of lead (Morveau). By reducing a slag containing lead and iron in a crucible lined with charcoal, Biewend (J. pr. Chem. xxiii. 252) obtained a well-fused alloy, which was hard, almost perfectly brittle, lustrous, and magnetic; it had a light steel-grey colour, a fine-grained laminar fracture, and contained 96·76 per cent. of iron and 3·24 of lead.

8. With Manganese.—Cast iron, alloyed with manganese, becomes white and more brittle; when the proportion of manganese amounts to 22 per cent. the iron ceases to exhibit magnetic properties. (Mushet.)

9. With Mercury.—An amalgam of iron with mercury is described by Joule. (Brit. Ass. Reports, 1850, p. 55.) See MERCURY.

10. With Molybdenum.—Molybdide of iron is bluish-grey, hard, brittle, fine-grained, and magnetic; fusible before the blowpipe when formed of equal parts of the two metals, but not so when formed of 2 pts. molybdenum and 1 pt. iron.

Many samples of the so-called "bears" (*Eisen-sauen*) which are metallic masses found in the hearths of blast furnaces in which copper is smelted, as at Mansfield (ii. 31), likewise consist of iron alloyed chiefly with molybdenum; *a*. Bear from the upper works at Eisleben, obtained in the fusion of bituminous marl-slate in smelting furnaces. *α*. Fine-grained. *β*. Coarse-grained (Heine, J. pr. Chem. ix. 176).—*b*. The so-called Magdeburg meteoric iron, containing slag mixed with bronze-yellow copper-cinder; probably the bear from a copper furnace. *α* is the analysis of a fine-grained sample, *β* of a coarse-grained sample, by Stromeyer (Pogg Ann. xxviii. 551); *γ* is the analysis by Wehrle (Zeitschr. Phys. v. W. iii. 168).—*c*. Bear found in the neighbourhood of the *rothe Hütte* in the Harz, examined by **Wiggens** (Pogg. xxviii. 565). *d.* Bear found underground at Lauchstadt. (**Steinberg**, J. pr. Chem. xviii. 379.)

	a, α.	*a, β.*	*b, α.*	*b, β.*	*b, γ.*	*c.*	*d.*
Iron . . .	57·91	73·26	74·60	76·77	73·11	81·14	50 to 80
Molybdenum . .	28·49	9·13	10·19	9·97	5·28	1·08	10 to 30
Manganese . .	. .	. .	0·01	0·02	0·12	0·14	
Cobalt . . .	0·67	0·77	3·07	3·25	4·16	2·40	trace
Nickel . . .	3·42	4·63	1·28	1·15	0·84	trace	1 to 6
Copper . . .	2·45	1·79	4·32	3·40	5·34	7·69	2 to 4
Silver . . .	. .	. .	. .	. .	trace		
Calcium . . .	. .	. .	. .	. .	. .	0·29	trace
Silicon . . .	. .	. .	0·39	0·35	1·83	1·94	
Carbon . . .	0·87	1·42	0·48	0·38	1·20	0·69	trace
Arsenic . . .	. .	. .	2·47	1·40	2·70	1·82	
Phosphorus . .	3·52	605	2·27	1·25	1·38	0·81	2 to 5
Sulphur . . .	0·60	009	0·92	2·06	2·94	0·62	trace
	97·93	97·14	100·00	100·00	98·90	98·62	

11. With **Nickel**.—Iron and nickel melt together with facility, forming alloys, some of which do not rust so easily as iron itself. An alloy of 1 pt. iron with 0·03 nickel is white, of specific gravity 7·80, as extensible as iron, and less liable to rust. 1 pt. iron with 0·1 nickel has a greyish-white to yellowish colour, specific gravity 7·85, is less extensible than iron, but rusts less easily. 1 pt. iron and 1½ pt. nickel form a grey, rather hard, perfectly extensible, and magnetic alloy.

Meteoric iron consists chiefly of an alloy of iron and nickel. (See p. 336; also METEORITES.)

12. With **Palladium**, iron forms a brittle alloy. (**Faraday** and **Stodart**, Phil. Trans. 1822, p. 254.)

13. With **Platinum**.—Equal weights of platinum and iron heated before the oxyhydrogen blowpipe unite, with vivid emission of sparks, and form a shining, very hard and malleable alloy, which is scarcely touched by the file. In equal volumes, the two metals yield a brittle button (**Clarke**). Combination does not take place in the heat of an ordinary fire (**Lewis**, **Gehlen**). An alloy of 99 pts. iron and 1 pt. platinum is not attacked by ordinary nitric acid. (**Schönbein**, Pogg. Ann. xlii. 17.)

When equal weights of iron and platinum are dissolved in nitromuriatic acid, the excess of acid expelled by evaporation, the solution precipitated by ammonia, and the washed precipitate reduced in a stream of hydrogen at a low red heat, an alloy of iron and platinum is obtained, which immediately takes fire on exposure to the air. If this alloy, without being allowed to come in contact with the air, so that no combustion may take place, be thrown into hydrochloric acid—which dissolves part of the iron with evolution of hydrogen—and the residue washed with water, there remains a black heavy powder, containing 80·1 per cent. platinum to 19·9 iron (which may be dissolved out by boiling nitric acid) together with a trace of moisture, but no hydrogen. This residue takes fire in the air considerably below a red heat, and burns with emission of sparks. Sometimes the combustion begins at the hottest part and spreads through the mass with a red light, as in the burning of tinder; after the combustion, the powder is found to have gained 1 per cent. in weight. (**Boussingault**, Ann. Ch. Phys. [2] liii. 441.)

Carbide of Platinum and Iron.—*α.* 9 pts. platinum and 2 pts. **steel** form a perfect alloy, which does not tarnish on exposure to the air; specific gravity 15·88. *β.* The alloy of 1 pt. platinum to 1 pt. steel takes a high polish, does not tarnish, exhibits a highly crystalline structure on the surface, and has a density of 9·862. *γ.* 1 pt. platinum and 8 pts. steel form a finely damasked alloy. *δ.* 1 platinum to 10 steel: specific gravity 8·1. *ε.* 1 pt. platinum to 67 pts. steel: the best adapted for cutting instruments. *ζ.* 1 pt. platinum to 100 pts. steel: of uniform surface, and beautiful fracture; not so hard as silver-steel, but much tougher, and therefore specially adapted to many purposes. *η.* 1 pt. platinum to 200 steel: damasked alloy, very well adapted for razors (**Bréant**). Steel alloyed with a small quantity of platinum dissolves in dilute sulphuric acid much more quickly than pure steel. This increase of solubility is produced even by $\frac{1}{400}$ pt. of platinum, and is strongest with a quantity between $\frac{1}{200}$ and $\frac{1}{100}$. With $\frac{1}{40}$ of platinum, the solubility is perceptibly less; steel alloyed with one-half platinum does not dissolve more quickly than pure steel; and a compound of 2 pts. steel with 9 platinum is not at all affected by dilute sulphuric acid. These alloys exhibit the same relations towards other dilute acids.

When a compound of 100 pts. of steel with 1 pt. of platinum (or of any other metal insoluble in nitric acid) is treated with dilute sulphuric acid, and the undissolved portion, containing platinum, iron, carbon, and hydrogen, is boiled with nitric acid, a black residue is left. This latter substance, when heated to 200°, detonates slightly, producing a faint light, but if gradually heated, decomposes with detonation; it dissolves in nitromuriatic acid, yielding a solution containing a larger portion of platinum, with but little iron. (**Faraday** and **Stodart**. Phil. Trans. 1822, p. 257, and Quart. Journ. of Science, p. 329.)

Cast iron and platinum form a dark, malleable, very hard alloy.

14. With **Potassium**.—An alloy having nearly the composition Fe^4K, is obtained by igniting 12 pts. iron filings with 8 pts. pulverised tartar; it has the aspect of bar-iron, is very hard; can be forged and welded, but oxidises very rapidly in air and water. (**Gay-Lussac** and **Thenard**, *Recherches Physico-chimiques*, i. 238; **Calvert**, Phil. Mag. Oct. 1855.)

15. With **Rhodium**.—1 pt. rhodium and 1 pt. steel form an alloy having a specific gravity of 9·176, and a very fine colour and surface for metallic mirrors; it does not tarnish in the air. An alloy of 1 pt. rhodium and 50 to 100 steel is very hard, tolerably tough, requires for tempering a temperature higher by 39° than common steel, and by 17° than Indian steel. (**Faraday** and **Stodart**, *loc. cit.* p. 329.)

16. With **Silver**.—Iron is said to take up a small quantity of silver when melted with it.

17. With **Tin**.—When iron and tin are heated to redness together, there is formed: *a.* An alloy of 22 pts. tin and 1 iron, somewhat harder than tin, and magnetic; and below it *b.* A compound of 2 pts. iron and 1 pt. tin (nearly Fe^2Sn), which is white, very hard, slightly malleable, and difficult of fusion: this constitutes *tinned Iron-plate.*—In cast-iron retorts in which the tin-amalgam used for silvering mirrors is continually distilled, for the purpose of regaining the mercury, an alloy of tin and iron is formed, amounting to between 1 and 2 per cent. of the tin obtained: when the tin is poured out of the retorts, this alloy partly floats upon it in scales, and is partly deposited at the bottom in the form of a doughy mass. It may be freed from the pure tin which adheres to it, either by boiling with hydrochloric acid, which dissolves the latter, or by treating it with nitric acid, by which the free tin is oxidised while the alloy is not attacked. When thus purified, it has the form of shining square needles, of specific gravity 8·733, brittle, and fusing at an incipient white heat. The powder of this compound, when thrown into the flame of a candle, burns with emission of sparks and a white smoke. It does not rust in the air, when moistened with water. It is not attacked by nitric acid at any temperature or any degree of concentration; it dissolves slowly in boiling hydrochloric acid; but rapidly and completely, and with violent action, in nitromuriatic acid. (**Lassaigne**, *J. Chem. méd.* vi. 609.)

Deville and Caron (Compt. rend. xlvi. 920) obtained the alloy Fe^2Sn,* in broad shining laminæ, which were but slightly attacked by hydrochloric acid.

An alloy containing FeSn remains in the preparation of stannous chloride from Banca tin (see TIN), in slender (probably quadratic) needles of specific gravity 7·44, fusible only at a white heat; it solidifies in the crystalline form on cooling, and is then magnetic. The crystals are nearly insoluble in hydrochloric and nitric acid, but dissolve easily in nitromuriatic acid; they burn in the flame of a candle. (**Nöllner**, Ann. Ch. Pharm. cxv. 233.)

It has been proposed to harden malleable iron rails by introducing a portion of tin into the metal, but it has been found to render the iron extremely brittle and "cold short," and also incapable of being welded. (**Karsten**, *Eisenhüttenkunde*, i. 508, and **Percy**, *Metallurgy*, ii. 161.)

18. With **Titanium**.—Pig-iron often contains titanium (p. 335), which appears to be derived chiefly from the clay of the ore, or from other siliceous compounds added as fluxes. In three samples of grey pig from the iron ore of Westbury in Wiltshire, Riley found 1·15, 0·71 and 0·47 per cent. titanium. The titanium is either minutely disseminated through the iron or else alloyed with it. The presence of titanium in the ore or in the flux appears to improve the quality of the iron, and render it of excellent quality both for castings and for conversion by the Bessemer process; but according to Riley's observations, the titanium does not appear to remain with the iron, at least only in very minute quantity, when it is converted into bar iron or steel. Mushet has patented the use of titanium in the manufacture of iron and steel, and the alloying of titanium with iron and steel; but samples of his steel, in the manufacture of which titaniferous ores were used, did not yield any appreciable evidence of titanium. (**Riley**, Chem. Soc. J. xvi. 387; see *ante*, p. 335.)

19. With **Tungsten**.—Iron and tungsten may be united by fusion. It is stated that steel of very superior quality may be made by simply melting cast steel, or even iron, either with metallic tungsten or with the so-called native alloy, prepared by

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* Fe = 28; Sn = 118.

strongly heating a mixture of powdered wolfram and fine carbonaceous matter in a crucible lined with charcoal. (Bernouilli, Pogg. Ann. 1860, xxi. 573.)

20. With Zinc.—Iron takes up zinc when heated with it. A brittle friable alloy is readily formed by melting zinc in vessels of wrought or cast iron, or by dropping iron into melted zinc; sometimes crystalline compounds of ferruginous zinc are deposited. (Percy, *Metallurgy*, ii. 153)

By immersing malleable iron or cast iron, perfectly free from oxide on the surface, in melted zinc, the iron becomes covered with a coating of zinc, probably in consequence of the two metals being alloyed superficially. Iron thus coated with zinc is less liable to undergo oxidation when exposed to the atmosphere, and is largely employed under the name of *galvanised iron*.

IRON, BROMIDES OF. Iron unites with bromine in two proportions, forming *ferrous bromide*, which is either a protobromide, FeBr, or a dibromide, $FfeBr^2$, according to the atomic weight of iron adopted, and *ferric bromide*, which in like manner is either a sesquibromide, Fe^2Br^3, or a tribromide, $FfeBr^3$.

Ferrous bromide is a yellowish substance obtained by passing bromine-vapour over gently ignited iron wire. It is soluble in water, and may be obtained in solution by dissolving iron in hydrobromic acid, or in a mixture of bromine and water. The solution yields by evaporation rhombic tabular crystals, containing $FeBr.3H^2O$. When exposed to the air it turns brown, and deposits *ferric oxybromide*.

Ferric bromide, Fe^2Br^3 or $FfeBr^3$, is produced by heating ferrous bromide with bromine, or by evaporating to dryness a solution of iron in excess of bromine-water. It is a brown-red mass which deliquesces in the air. It may be obtained in solution by dissolving ferric oxide in hydrobromic acid, or by mixing the aqueous solution of the ferrous bromide with bromine.

IRON, CARBIDES OR CARBURETS OF. See CAST IRON (p. 329) and STEEL. By heating alkaline ferrocyanides to redness, a compound of carbon and iron is obtained, consisting of FeC (FeC^2)?

Three other definite compounds of iron and carbon have been supposed to exist, viz. FfeC (or FeC), $FfeC^2$ (or FeC^2) and Ffe^4C (or Fe^4C), according to Karsten and Berthier (Ann. des Mines [3] iii. 229). More recently Gurlt (Chem. Gaz. xiv. 230) has endeavoured to show that there is another carbide, represented by the formula Ffe^3C (or Fe^3C). The nearest approach to a definite compound of carbon and iron is specular iron, which may perhaps consist essentially of a tetracarburet; but the evidence of the existence of these compounds is exceedingly imperfect.

IRON, CARBONATE OF. See CARBONATES, i. 784.

IRON, CARBURETTED, ANALYSIS OF. It has already been mentioned that cast iron contains, besides carbon, which is an essential constituent of it, a considerable number of other elements, both metallic and non-metallic, that many of these elements are not completely removed in the processes to which the iron is subjected to convert it into bar iron and steel, and that all of them have more or less influence on the quality of the iron. It becomes, therefore, an important problem to detect these several elements in iron, and, as far as possible, to estimate their amount.

The iron used for the analysis must be finely divided, as in the form of filings, turnings, or borings; very hard iron, such as specular iron, or hard steel, may be comminuted in a steel mortar, and sifted. The iron must of course be free from dust, rust, oil, and other foreign substances.

1. *Estimation of the entire amount of Carbon.*—To estimate the whole of the carbon in iron, both free and combined, the iron must be dissolved, without evolution of hydrogen, because that gas would carry some of the carbon with it; or the carburetted iron must be completely oxidised, and the carbon estimated as carbonic acid.

When carburetted iron is brought in contact with *chloride of silver*, *cupric chloride*, or *ferric chloride*, these compounds are reduced to metallic silver, cuprous chloride, and ferrous chloride respectively, while the metallic iron is also converted into ferrous chloride, which dissolves, and the whole of the carbon remains behind, together with silicon and various metals. The action of chloride of silver is very slow; the most convenient reagent for this purpose is *cupric chloride*. A quantity of the iron (5 to 10 grms.) is covered with a moderately concentrated aqueous solution of cupric chloride, free from excess of acid, whereupon metallic copper is precipitated, and ferrous chloride is formed. As soon as trituration with a glass rod shows that the deposit is free from hard particles of iron, the solution is decanted and the residue is drenched with a concentrated solution of cupric chloride acidulated with hydrochloric acid, in order to convert the reduced copper into cuprous chloride, and dissolve it. The solution is then filtered through a glass tube drawn out at the lower end to a narrow neck, and plugged with asbestos (or platinum-sponge), so as to retain all undissolved particles. Impure carbon is thus obtained, the weight of which may be determined by weighing the tube dried at 124°–130° C., both before and after the experiment.

Ferric chloride may also be used instead of cupric chloride, the free acid contained in the solution being previously neutralised with carbonate of sodium or carbonate of calcium. The basic ferric salt deposited in the reaction may be removed by dilute hydrochloric acid or solution of ferric chloride.

The iron may also be dissolved, without loss of carbon, by nitric acid, provided it be first drenched with water, and then nitric acid free from chlorine or nitrous acid added. As soon as the solution has attained a sufficient degree of concentration, it is poured off, the residue is drenched with fresh quantities of water and aqueous acid, and the turbid yellowish solution, which contains nitrate of ammonia and nitrate of iron, is left to clarify, and finally filtered as above.

Another method is to heat the finely divided iron in a stream of dry *chlorine gas*, previously freed from air by passing through a red-hot tube containing finely divided charcoal.

Bromine or *iodine* may also be used instead of chlorine, and in the wet way, Morfitt and Booth (Chem. Gaz. 1853, p. 358) drench the iron (not very finely divided) with a small quantity of water, add iodine (5 grms. to 1 grm. iron), and leave it for five or six hours, till the action is finished; then pour off the liquid, add more water and iodine, if any iron still remains, and filter. Care must be taken not to add too much water, and not to allow the action to go on too long, otherwise a portion of the carbon will be lost. The charcoal which remains after the solution of iodide of iron has been filtered off, is washed with hot water, then with hydrochloric acid, and again with water, and the residue is weighed.

The carbon obtained by either of these methods is not pure, but is mixed with a small quantity of iron, and a larger quantity of silicic anhydride and oxide of silicon. The amount of pure carbon may be determined, either by the loss which the residue sustains when ignited in contact with the air, or by burning the carbon as in organic analysis, with oxide of copper, or better with chromate of lead, or with a mixture of that salt and chlorate of potassium, or in a stream of oxygen, and weighing the carbon as carbonic anhydride by absorption in caustic potash.

Deville (Compt. rend. li. 938) separates the pure carbon at once by igniting the finely divided iron in a current of dry hydrochloric acid gas, quite free from atmospheric air. The iron and all the foreign constituents, except the carbon, are then converted into volatile chlorides, and pure carbon remains behind.

2. *Estimation of the Graphite or mechanically mixed carbon.*—This is the portion which remains behind mixed with silica, and sometimes also with humus-like carbon-compounds, when the iron is dissolved by dilute acids. To estimate it, the iron is dissolved out by dilute hydrochloric acid of specific gravity 1·1; the washed residue is digested in potash-ley of specific gravity 1·1, to remove silica and humus-compounds, then with water, then with hot hydrochloric acid, and lastly, with hot water, after which it is dried, weighed and ignited in contact with the air, the loss of weight which it then sustains being reckoned as graphite (Morfitt and Booth). Buchner (J. pr. Chem. lxxii. 364) washes the residue with boiling water, potash-ley, alcohol, and finally with ether; then dries, weighs, and ignites as above. Gurlt (Polyt. Centralblatt, 1856, p. 378) treats the finely divided iron with recently precipitated chloride of silver and solution of sal-ammoniac, digests the residue with cyanide of potassium to remove chloride of silver, with potash to remove silica and combined carbon, then with nitric acid to remove metallic silver: the residue consists of graphite, which is to be treated as above.

3. *Estimation of the combined Carbon.*—The carbon actually in combination with the iron is for the most part converted, during the solution of the metal, into volatile hydrocarbons, which escape with the hydrogen, and impart to it a well-known offensive odour; part of this carbon, however, always remains in the liquid form attached to the graphite. When carburetted iron is digested with *chloride of silver*, ferric chloride, or cupric chloride, as already described, the whole of the carbon remains behind, and on treating the residue with potash-ley, that which was originally combined with the iron dissolves, and may be separated, together with silica, by supersaturation with hydrochloric acid, evaporation to dryness, and washing. The amount of carbon in the residue thus obtained may then be determined, either by the loss of weight sustained on ignition, or by combustion with chromate of lead. The combined carbon is, however, more generally estimated by difference.

4. *Estimation of Silicon.*—The amount of this element may be determined by igniting the residue obtained in the preceding operation; the carbon then burns away, and silica remains behind; as, however, a small portion of the carbon is apt to escape combustion, and the residue likewise contains a certain portion of slag, the pure silica must be dissolved out by potash-ley of specific gravity 1·1 (which will not attack the slag), and then precipitated by supersaturation with hydrochloric acid.

Caron ignites the pulverised iron in a mixture of hydrochloric acid and air, whereby the carbon is converted into carbonic anhydride, and the iron into volatile chloride, while silica remains, sometimes mixed with the oxides of titanium, aluminium, calcium, &c.

The silicon in iron also remains as silica in the residue left on burning the iron in a stream of oxygen, and may be separated by moistening this residue with concentrated hydrochloric acid, evaporating to dryness, then digesting in dilute hydrochloric acid and filtering.

5. *Estimation of Nitrogen.*—The nitrogen may be detected in cast iron, according to Marchand, by igniting the finely divided iron with potassium, perfectly cleansed from oil and well dried, in an atmosphere of hydrogen quite free from air. The resulting mass, dissolved in water, yields, on addition of a ferroso-ferric salt and supersaturation with hydrochloric acid, a precipitate of prussian blue. According to Frémy, the nitrogen of iron may be converted into ammonia by ignition in pure hydrogen.

The nitrogen may be estimated by igniting the pulverised iron with six times its weight of a mixture of caustic lime and baryta, receiving the ammonia thus evolved in hydrochloric acid, and converting it into platinum-salt. Another method is to dissolve the iron in acid, whereupon ammonia remains in solution; boil the liquid with excess of slaked lime, and receive the vapours in hydrochloric acid. A portion of the nitrogen may, however, remain in the carbonaceous residue, and may be determined by igniting that residue with soda-lime in the ordinary way.

6. *Estimation of Sulphur.*—The sulphur in pig iron may be converted into sulphuric acid by oxidation with nitric acid, but the quantity is generally too small to be estimated in this way. A better method is to convert it into sulphydric acid, by dissolving the iron in dilute hydrochloric acid (which, of course, must not contain sulphurous acid, or free chlorine), and pass the evolved gas through a Liebig's bulb-apparatus containing an ammoniacal solution of nitrate of silver, or through a series of small flasks containing chloride of copper, or acetate of lead (the latter mixed with acetic acid), and weigh the precipitated sulphide: 100 pts. sulphide of silver = 12·91 sulphur; 100 pts. sulphide of copper = 13·45 sulphur. As, however, the precipitated sulphide may also contain phosphide or arsenide, it is better to oxidise the sulphide with nitric acid, and precipitate the resulting solution with chloride of barium.

Another mode of estimation is to fuse the pulverised iron with nitre and carbonate of sodium, dissolve the mass in dilute hydrochloric acid (silica then remaining undissolved), and precipitate the sulphuric acid as a barium-salt. If the fusion is conducted over a gas-flame, care must be taken that the mass does not pass over the edge of the vessel, because in that case the sulphurous acid in the flame, coming in contact with the fused alkali, will be oxidised, and form an alkaline sulphate, which will greatly increase the apparent amount of sulphur in the iron. If the fusion is made over a spirit-lamp, this source of error does not arise. (D. S. Price, Chem. Soc. J. xvi. 51.)

In several of the analyses already given (pp. 332, 333), the estimation of sulphur is probably too high. The results that are questionable are marked *.

7. *Estimation of Phosphorus.*—The iron (5 to 10 grms.) is dissolved in nitric or nitromuriatic acid; the solution evaporated to dryness; the dry residue fused with three or four times its weight of alkaline carbonate; the fused mass disintegrated by water; the filtrate supersaturated with hydrochloric acid and evaporated to dryness to separate silica; the residue digested in water; and from the filtrate the phosphoric acid is precipitated as ammonio-magnesian phosphate. The acid filtrate may also be previously used for the estimation of sulphuric acid, the excess of baryta added being then removed, previously to precipitating the phosphoric acid in the way just mentioned. If the solution also contains alumina, tartaric acid must first be added, to hold that base in solution.

The nitric acid solution of the iron may also be precipitated in the cold with carbonate of sodium; the whole of the phosphorus is then thrown down as ferric phosphate, which, after washing, may be fused with alkaline carbonate and treated as above, or decomposed by sulphide of ammonium.

The iron filings may also be fused at once with a mixture of alkaline carbonate and nitrate; the fused mass treated as above described for the estimation of sulphuric acid; and the solution, after being freed from silica, may be used either immediately or after separation of the sulphuric acid, for the estimation of phosphoric acid.

Eggertz (J. pr. Chem. lxxix. 496), evaporates to dryness the solution of 1 grm. iron in 15 grms. nitric acid of specific gravity 1·2, moistens the mass with hydrochloric acid, and dissolves it in such a quantity of water, that the filtrate measures 15 c. c., then adds 12·5 c. c. of a solution of molybdic acid (prepared by dissolving 1 pt. molybdic acid in 4 pts. ammonia, pouring the quickly filtered liquid into 15 pts. nitric acid, and leaving it to settle). On leaving the mixture to itself for a few hours at 40°, a precipitate forms, which must be collected on a weighed filter, washed with water containing 1 per cent. of nitric acid, and dried at 95°. 100 pts. of the dried precipitate correspond to 1 pt. phosphorus.

8. *Estimation of Arsenic.*—When arseniferous iron is dissolved in dilute hydrochloric or sulphuric acid, the arsenic is not given off as arsenetted hydrogen, but is converted into arsenic acid (H. Rose), which remains dissolved if the solution has been made in the cold, but is precipitated from warm solutions not containing too great an excess of acid, as basic ferric arsenate, and is therefore often found in the carbonaceous residue.

When the iron is dissolved in nitric or nitromuriatic acid, the arsenic is converted into arsenic acid, and may be precipitated as basic ferric arsenate (together with phosphate) by boiling the solution with acetate of sodium, after the greater part of the ferric oxide has been reduced to ferrous oxide by heating it with sulphite of sodium. The precipitate is then decomposed by sulphide of ammonium, and the filtrate, acidulated, and treated with sulphydric acid, yields a precipitate of sulphide of arsenic. Or the iron may be dissolved in hydrochloric acid, with addition of a little nitric acid, to dissolve all the arsenic; the filtrate heated with sulphite of sodium, to reduce all the ferric to ferrous chloride; and the solution, freed from excess of sulphurous acid, may be treated with sulphydric acid, with the usual precautions; the arsenic is then precipitated as trisulphide (together with the sulphides of copper and lead, if present).

As a portion of the arsenic sometimes remains in the carbonaceous residue, this residue must be examined, either by treating it with sulphide of ammonium, and precipitating the arsenic from the filtrate by sulphydric acid, or by fusing it with nitrate and carbonate of sodium, and precipitating the arsenic as ammonio-magnesian arsenate.

The pulverised iron may also be fused with nitrate and carbonate of sodium, the silicic and sulphuric acids separated as above, and the arsenic then precipitated by sulphydric acid, or if no phosphorus is present, by ammonia and sulphate of magnesium.

9. *Estimation of Manganese, Cobalt, Nickel, and Zinc.*—These metals may all be separated from iron, by precipitating the latter from a neutral solution in which all the iron exists as ferric salt, with benzoate or succinate of ammonium, or from acid solution, with carbonate of barium.

10. *Estimation of Copper and Lead.*—The precipitate, thrown down as above described by sulphydric acid from the reduced iron solution, sometimes contains traces of these two metals. The arsenic may be extracted from it by monosulphide of potassium; and the residue, oxidised with nitric acid and treated with sulphuric acid, yields insoluble sulphate of lead and a soluble copper salt.

11. *Estimation of Aluminium.*—For the method of separating this metal from iron, see i. 155.

12. *Estimation of Magnesium, Calcium, and the Alkali-metals.*—These metals remain in solution after the iron has been precipitated as ferric oxide by benzoate or succinate of ammonium, or by carbonate of barium, and may be separated and estimated by the usual methods.

13. *Estimation of Chromium, Vanadium, Titanium, Molybdenum, and Tungsten.*—These metals occur especially in the black residue which remains when pig iron is dissolved in dilute acids, and may be sought for either in this or directly in the iron.

To detect and separate chromium and vanadium, a large quantity of the pulverised iron is fused with 12 pts. nitrate and 1 pt. carbonate of sodium; the fused mass (which likewise contains silicic, phosphoric, and arsenic acids) is mixed with such a quantity of nitric acid that it still retains a slight alkaline reaction, but does not give off any nitrous acid (which would reduce the chromic and vanadic acids); the solution is mixed with chloride of barium; the washed precipitate is treated with sulphuric acid; the solution is saturated with ammonia and evaporated; and a lump of sal-ammoniac is thrown in, whereby vanadate of ammonium is thrown down as a yellow or white crystalline powder, while the chromate remains in solution. The vanadate of ammonium, heated in contact with the air, yields dark red vanadic acid, the quantity of which can then be determined.

According to Sefström, the vanadic (and chromic) acid may be separated from the fused mass, after neutralisation with nitric acid, by the addition of a lead-salt; the washed precipitate is then boiled with strong alcohol and hydrochloric acid, the resulting blue solution of vanadic (and chromic) oxide, after being evaporated, is oxidised by nitric acid or chlorine-gas, then mixed with potash-ley, evaporated down, and fused; the fused mass is dissolved in water; and the vanadic acid is precipitated, as above, by sal-ammoniac. The liquid filtered therefrom (after separation of phosphoric and arsenic acids as ammonio-magnesian salts) yields with sulphydric acid a precipitate of chromic hydrate, while sulphide of molybdenum remains in solution, whence it may be precipitated by acids, and, when fused in a narrow tube, yields pure sulphide of molybdenum.

According to Müller, the mass obtained by fusing the iron with nitre and soda, may be dissolved in water, the filtrate treated with chlorine-gas, which separates phosphate of aluminium, and then saturated with nitric acid, afterwards with ammonia, and the vanadium precipitated by sal-ammoniac—or the fused mass is boiled with excess of sulphide of ammonium, or saturated with sulphydric acid gas (whereby chromic oxide and alumina are separated), and sulphide of vanadium precipitated from the solution of the alkaline sulphovanadate by an acid.

The chromic acid may be separated from the liquid filtered from the vanadate of ammonium by the ordinary methods, and most readily detected, after addition of pure nitric acid, by its reaction with peroxide of hydrogen (i. 953). The chromic acid may also be precipitated from the alkaline liquid, after neutralisation with nitric acid, by means of mercurous nitrate, the phosphoric and arsenic acids having first been precipitated by ammonia and nitrate of magnesium (the addition of sal-ammoniac and sulphuric acid must be avoided, as they would precipitate the mercurous salt).

Riley (Chem. Soc. J. xvii. 23) separates vanadium from pig-iron by dissolving the borings in dilute hydrochloric acid, and after the iron is nearly all dissolved, adding a strong acid, and boiling well; the chloride of iron is then filtered off from the graphite and silica; the filter well washed from chloride of iron, and treated with a dilute solution of potash to dissolve the silica; the potash thoroughly washed out; and the filter treated with hydrochloric acid, washed until all the acid is removed, then dried, ignited, and burnt over a Bunsen's burner, or better in a muffle. The residue is a semi-fused mass, apparently consisting of a mixture of a fusible and infusible oxide, staining a porcelain crucible yellow, and adhering strongly to it, some portions of the mass being of a purply blue colour, similar to the bloom of a plum.

The semi-fused residue, treated with concentrated hydrochloric acid, gives off chlorine, and forms a yellowish-brown solution, which on boiling soon becomes of a beautiful green colour, leaving a black, finely pulverulent, insoluble residue. The solution, freed from excess of acid by evaporation, leaves a syrupy dark green mass, which when heated with water, yields a small quantity of white insoluble flocculent matter, and a solution which has a green colour when acid, but blue when nearly neutral or largely diluted, and gives the characteristic reactions of vanadium-salts, especially the yellow precipitate, becoming greenish on standing, with ferrocyanide of potassium.

The black insoluble residue, fused with acid sulphate of potassium, forms a mass which dissolves perfectly in cold water, and yields on boiling a dense yellowish-white pulverulent precipitate, exhibiting the reactions of vanadium-salts. The black powder appears to be vanadous oxide, and the soluble portion of the original residue consists chiefly of vanadic acid. In a sample of grey pig iron from Westbury in Wiltshire, also containing a considerable quantity of phosphorus, part of which passed, as phosphoric acid, into the residue insoluble in dilute acids, Riley found—by separating the phosphoric acid from this residue as magnesium-salt, and considering the remaining portion soluble in concentrated hydrochloric acid, as vanadic acid—that the total quantity of vanadic acid in the pig was 0·686 per cent.

Molybdenum sometimes occurs in the carbonaceous residue left on dissolving pig iron in acids, and may be dissolved out together with arsenic, by sulphide of ammonium, and precipitated therefrom by acids: on heating the precipitate in a glass tube, sulphide of molybdenum remains behind.

Iron rich in molybdenum, such as the "bears" from copper furnaces (p. 367), may be dissolved in nitromuriatic acid; the solution evaporated to dryness after addition of hydrochloric acid; then redissolved and precipitated by sulphydric acid, with addition of metallic zinc. The whole of the molybdenum is thus precipitated, and may be separated from other metals by solution in sulphide of ammonium, precipitation therefrom by acids, and heating.

Titanium is obtained as titanic acid [anhydride] when pulverised iron is heated in a current of hydrochloric acid gas and oxygen; it then remains, together with silica, alumina, lime, &c., and may be rendered soluble by fusion with carbonate of sodium.

When iron is dissolved in nitric acid, at last with aid of heat, and the solution is evaporated to dryness and redissolved in nitric acid, titanic anhydride remains, together with carbon, silica, &c., and may be rendered soluble as above.

The iron may also be dissolved in cold hydrochloric acid, the solution mixed with tartaric acid to prevent the precipitation of the iron by ammonia, and the whole of the iron (together with cobalt, nickel, copper, &c.) precipitated by sulphide of ammonium; titanic acid then remains in solution, and may be precipitated and estimated by methods which will be described under TITANIUM.

Riley (Chem. Soc. J. xv. 391), after dissolving the iron in hydrochloric acid, collects the residue on a weighed filter, treats the residue with dilute potash to dissolve out the silica, and after washing the filter with hydrochloric acid, dries it at 250°, and weighs it. The weight of the residue, consisting of graphite mixed with titanic anhydride, being thus determined, the graphite is burnt off, and the dirty light brown residue is fused with acid sulphate of potassium; the fused mass dissolved in cold water; and the solution boiled, whereupon titanic anhydride is precipitated nearly pure. Part of the titanium is, however, dissolved by the acid together with the iron: hence, to obtain the entire amount, the solution obtained by fusing the residue from the silica with acid sulphate of potassium must be added to the iron solution, after the sulphur contained in it has been precipitated as a barium-salt, and the excess of baryta removed. The solution in which the titanium and phosphorus are to be determined, is first reduced with sulphite of sodium, and the excess of sulphurous acid driven off. It is then nearly neutralised with ammonia, and acetate of sodium or ammonium added. If there is only a small quantity of phosphoric acid present, there will always be sufficient ferric oxide to precipitate it; but if not, a few drops of nitric acid must be added, and the solution boiled and filtered as quickly as possible. This precipitate may be at once treated; or if it contains much ferric oxide, in excess of that sufficient to form phosphate of iron, it is better to redissolve it in hydrochloric acid, reduce it again with sulphite of sodium, and repeat the operation above described. The precipitate is then dissolved in hydrochloric acid, and chloride of magnesium, ammonia, chloride of ammonium, and tartaric acid added, the precipitate produced being allowed to stand two nights; then the ammonio-magnesiam-phosphate is filtered off, dried, ignited, and weighed, and the phosphoric acid calculated from the pyro-phosphate of magnesium. The filtrate from the phosphoric acid is treated with sulphide of ammonium, and the sulphide of iron separated, the filtrate evaporated to dryness, ignited, and burnt in a muffle; or evaporated nearly to dryness, transferred to a flask, and treated with fuming nitric acid until all the tartaric acid is destroyed; in either case, the residue is fused with acid sulphate of potassium. The fused mass is dissolved in cold water, boiled for some hours, and allowed to stand a night in a warm place, when the titanic acid is filtered off and washed with dilute sulphuric acid—dried, ignited, and weighed. If the determination of phosphoric acid is not required, then the precipitate produced (either by one treatment or two) by the alkaline acetate, may be dried (without washing), burnt, and fused with acid sulphate of potassium, and dissolved in cold water, whereby a little phosphate of iron, which remains insoluble, is separated; and the solution being boiled, the titanic acid is precipitated, and may be separated as before. (For further details, see the paper above referred to.)

Tungsten, which sometimes occurs in the residue of the solution of iron in hydrochloric acid, may be rendered soluble by fusion with alkaline carbonate, and separated by precipitation with acids or with mercurous nitrate. It may be separated from the other constituents of the iron by the solubility of tungstic acid in ammonia, or of the sulphide in sulphide of ammonium.

14. *Estimation of the Iron.*—The amount of pure iron in carburetted iron is generally determined merely by difference, after all the other constituents have been estimated. It may, however, be estimated directly by Fuchs' method with metallic copper (p. 383), or by any of the volumetric methods hereafter to be described. Mohr recommends especially the use of two titrated solutions of chromate of potassium, one ten times more dilute than the other (p. 384).

IRON, CHLORIDES OF. Iron forms with chlorine two compounds, analogous to the bromides.

Ferrous Chloride, FeCl or $FfeCl^2$, is obtained in the anhydrous state:—1. By passing chlorine or hydrochloric acid gas over iron filings or turnings heated to redness in a gun-barrel connected with a receiver into which the product may sublime.—2. By heating iron-filings with sal-ammoniac, ferrous chloride then remaining behind.—3. By boiling down a solution of iron in hydrochloric acid out of contact with the air, and heating the residue till the water is expelled.

Ferrous chloride crystallises in white or yellowish-white shining scales, which, according to Senarmont, are six-sided, and optically uniaxial; it has a specific gravity of 2·528, melts at a red heat, and sublimes when more strongly heated in a close vessel. Heated in an atmosphere of *hydrogen*, it is reduced, yielding hydrochloric acid and pure iron crystallised in cubes. Heated in dry *air* or *oxygen gas*, it is resolved into ferric oxide and chloride, the latter volatilising:

$$3FfeCl^2 + O^3 = Ffe^2O^3 + 2FfeCl^3.$$

In contact with *aqueous vapour* at a red heat, it gives off hydrogen and hydrochloric acid, and is converted into ferroso-ferric oxide:

$$3FfeCl^2 + 4H^2O = Ffe^3O^4 + 6HCl + H^2.$$

It absorbs *ammonia-gas* at ordinary temperatures, swelling up and crumbling to a white powder, which, when exposed to the air, quickly takes up water and oxygen, and is converted into ferric oxychloride and ferrico-ammonic chloride. Ferrous chloride, heated to redness in dry ammonia gas, is converted into a nitride of iron, Ffe^4N^2, containing 9·3 per cent. nitrogen (Frémy, Compt. rend. iii. 323). When mixed with a little charcoal powder, it is reduced by zinc-vapour at a red heat, yielding crystalline metallic iron, sometimes in dendrites, sometimes in tetrahedrons, and of specific gravity 7·84. (Ponmarède, Compt. rend. xxix. 520.)

Ferrous chloride exposed to moist air, absorbs water, and deliquesces. It dissolves easily in *water* and *alcohol*, but is insoluble in *ether*. It dissolves in 2 pts. water at 81·75° (Abl, Oesterreich. Zeitschr. f. Pharm. viii. 20); in 1 pt. of strong alcohol at 82·5°. (Wenzel.)

Hydrated Ferrous chloride, $FeCl.2H^2O$ or $FfeCl^2.4H^2O$, is most easily obtained by dissolving iron in aqueous hydrochloric acid, finally heating the solution with excess of metal, and filtering it at the boiling heat into a vessel moistened with strong hydrochloric acid. The bluish-green liquid, left to cool in well-closed vessels, deposits the hydrated chloride in crystals, which must be quickly pressed between paper and dried in air at about 30°. The bluish crystals are monoclinic, and cleave parallel to $\infty P\infty$ and $+P$. Specific gravity, 1·937. The salt may be obtained as a crystalline powder by concentrating the solution in a flask or a retort, and evaporating the concentrated liquid over the water-bath to a paste, stirring till it is cold. The crystals heated in a close vessel first give off half their water, and the remainder at a higher temperature; when quickly heated, they melt in their water of crystallisation; they effloresce at ordinary temperatures when kept over oil of vitriol. They dissolve in 0·68 pts. *water*, easily in *alcohol* and, according to most authorities, in *ether;* according to Jahn, however, they are insoluble in ether. The solutions, especially the alcoholic, absorb *nitric oxide* gas, and assume a black-brown colour. The aqueous solution yields by *electrolysis*, iron and hydrogen at the negative, chlorine and oxygen at the positive pole.

Ferrous chloride forms double salts with the chlorides of the alkali-metals. A mixture of the concentrated solutions of ferrous chloride and *chloride of potassium* yields, by cooling or slow evaporation, the salt, $KCl.FeCl.H^2O$ or $2KCl.FfeCl^2.2H^2O$, in pale blue-green monoclinic crystals. A similar *ammonium-salt* is obtained by mixing the corresponding solutions, or by boiling iron filings with sal-ammoniac, hydrogen and ammonia being then set free.

Ferric Chloride. *Sesqui-* or *trichloride of Iron*, Fe^2Cl^3 or $FfeCl^3$, also called *Perchloride of Iron*, *Iron sublimate.*—This compound is sometimes found in the craters of volcanos; it may be obtained artificially by the following processes:—1. A piece of iron wire or a watch-spring introduced red-hot, or with a piece of burning tinder at the end, into chlorine gas, burns with a red glow and forms ferric chloride, which then sublimes. The same result may be obtained by passing chlorine gas over gently heated iron.—2. Ferrous chloride heated in chlorine gas is converted into ferric chloride.—3. When ferrous chloride is heated in a vessel containing air, ferric chloride sublimes, and ferric oxide remains behind.—4. When an aqueous solution of ferric chloride is evaporated, the dry compound remains behind, mixed with more or less ferric oxychloride; the dry residue, gently ignited in a loosely closed flask, yields the ferric chloride sublimed in laminæ.—5. A mixture of 1 pt. calcined ferrous sulphate, and 1 pt. chloride of calcium, is ignited in a flask till the ferric chloride sublimes. (Baur, Repert. Pharm. xxv. 432.)

Ferric chloride forms iron-black, iridescent plates, having a metallic lustre, and volatilising and subliming somewhat above 100°. When heated in contact with *oxygen gas*, it yields ferric oxide and chlorine; heated with aqueous vapour, it forms ferric oxide and hydrochloric acid gas. With *sulphuric acid* and with *sulphur*, it behaves like ferrous chloride. (A. Vogel.)

Hydrated Ferric chloride.—Ferric chloride dissolves in water with considerable evolution of heat, and likewise deliquesces in the air. The liquid formed by deliquescence is called *Oleum Martis*. The same solution may be obtained by the following methods:—1. By dissolving ferric oxide or its hydrate in boiling hydrochloric acid.—2. By dissolving iron to saturation in a definite quantity of hydrochloric acid; filtering the solution, and mixing it with half as much hydrochloric acid as it already contains; then heating the liquid to ebullition in a capacious vessel, and adding nitric acid in small portions, till the dark-brown colour first produced by the absorption of nitrous gas has given place to a yellowish-brown, and the further addition of nitric acid produces no evolution of nitrous gas. The mixture is very apt to froth over, especially towards the end of the operation, when all the nitric oxide which has been absorbed has been evolved. The same result may also be obtained by dissolving iron in nitromuriatic acid; but it is not easy to hit the right proportion of the acids.—3. By passing washed chlorine gas through aqueous hydrochloric acid saturated with iron, as long as the gas is absorbed. The dark brown liquid, which has a rough taste and colours the skin yellow, yields, on evaporation and cooling, crystals containing two, or perhaps three different proportions of water.

a. Hex-hydrated, $Fe^2Cl^6.6H^2O$ (with 40 per cent. water).— Ferric chloride deliquesces rapidly in the air, then crystallises in the form of this hydrate, and afterwards deliquesces much less quickly (Kinast, Kastn. Arch. xx. 231). The same hydrate likewise separates slowly from an aqueous solution of the chloride not too much concentrated—fine radii stretching out in all directions from particular points, and forming pale orange-yellow, opaque, hemispheric nodules, into which the whole liquid is ultimately converted. If the evaporation has been carried too far, the syrup will not crystallise unless it be exposed for some time to the damp air of a cellar, from which it can absorb water. (Mohr, Ann. Ch. Pharm. xxix. 173.)

β. A $\frac{5}{2}$-hydrate, $2Fe^2Cl^6.5H^2O$ (with 21·7 per cent. water) is obtained by evaporating the liquid to a syrup, mixing it with a small quantity of strong hydrochloric acid to re-dissolve the precipitated ferric oxychloride, and leaving it to itself in the cold (Stein, Repert. Pharm. xiii. 264).—2. By fusing the crystals *a*, evaporating till the liquid becomes perfectly solid on cooling, replacing the lost hydrochloric acid, and leaving the solution to cool (Fritzsche).—3. The crystals *a*, placed beside oil of vitriol, under a receiver containing air, soon deliquesce and form a thick liquid, in which large crystals then form, till the whole is converted into a mass of crystals (Fritzsche, J. pr. Chem. xviii. 479). The $\frac{5}{2}$-hydrate forms flat roseate or deep reddish-yellow crystals, which fuse readily, and solidify again at 42°; they absorb water from the air very rapidly, and with evolution of heat (Fritzsche). When the crystals *a* and *β* are shaken together, a slight fall of temperature takes place, and a liquid is obtained—the same as that produced by imperfect evaporation of the crystals *a*—which produces great heat when mixed with water (Fritzsche). 2 at. ferric chloride dissolved in 9 at. water yields a liquid, which is identical with the *Oleum Martis* of the older chemists (as obtained by deliquescence of the solid chloride in the air), has a density of 1·545, and refuses to crystallise. Hence there are two solutions of ferric chloride in water to be distinguished; one containing more than $\frac{5}{2}$ and less than 6 at., the other containing more than 6 at. water.

Tri-hydrate, $Fe^2Cl^6.3H^2O$ (with 25 per cent. water)?—The hydrate is obtained, according to Wittstein, by leaving a solution of ferric chloride concentrated to a density of 1·50 in a covered plate, standing in a cool place, till it solidifies to a mass of rhombic plates; also by evaporating to a syrup and leaving it in a covered vessel in a warm place. According to Gobley, Mohr, and Fritzsche, however, highly concentrated solutions of ferric chloride always yield the $\frac{5}{2}$-hydrate.

Hydrated ferric chloride dissolves easily in *alcohol* and *ether*, forming yellow solutions, in which, however, if exposed to light or heat, especially in the ethereal solution, it is easily reduced to ferrous chloride. Ether abstracts it from the aqueous solution.

Ferric chloride is also easily reduced to ferrous chloride by *zinc*, *stannous chloride*, *sulphurous acid*, *sulphydric acid*, &c. *Hydriodic acid* reduces the concentrated, but not very dilute solutions of ferric chloride. *Silver* and *platinum*, immersed in the solution, are converted into chlorides, reducing the ferric to ferrous chloride. The reduction is likewise effected by many *organic bodies*. The reducing action of *tartaric acid* on ferric chloride has been applied to photographic purposes by Poitevin. (Compt. rend. lii. 94.)

A concentrated acid solution of ferric chloride yields by *electrolysis*, ferrous chloride at the negative pole, while chlorine, and a small quantity of oxygen are evolved at the positive pole. Liebig has suggested the use of this solution, instead of nitric acid, in the zinc-carbon battery; the zinc, according to Buff, should then be immersed in solution of common salt. Such a circuit is, however, less powerful than that of Bunsen.

Ferric chloride is much used in medicine; it is a powerful styptic, and is employed in the treatment of aneurisms and varicose veins. A few drops of the aqueous solution quickly coagulate albumin. (Handw. d. Chem. ii. [3] 607.)

Basic Ferric Chloride, or *Ferric Oxychloride*.—When a solution of ferric chloride is evaporated, hydrochloric acid, resulting from mutual decomposition of the ferric chloride and water, is always given off at a certain degree of concentration; at the same time a certain quantity of undecomposed ferric chloride volatilises, and a basic salt is left, consisting of ferric chloride with more or less ferric hydrate. The stronger the concentration, the greater is the quantity of basic salt in the residue. The evaporated mass no longer dissolves clearly in water, unless hydrochloric acid is added to reconvert the ferric hydrate into chloride. If the temperature be raised very high during the evaporation, a considerable quantity of ferric chloride is evolved, and a highly basic insoluble salt remains behind. A solution of ferric chloride heated to 300° in a sealed tube, deposits ferric oxide. (Senarmont.)

Insoluble ferric oxychlorides of variable constitution are likewise obtained by exposing a solution of ferrous chloride to the air; by precipitating a solution of ferric chloride with a quantity of alkali not sufficient to take up the whole of the chlorine; and by roasting iron in contact with metallic chlorides, chloride of sodium for example, all these compounds when heated, give off water, and afterwards ferric chloride, leaving ferric oxide.

Soluble ferric oxychlorides, or basic chlorides, are obtained by adding recently precipitated ferric hydrate to aqueous ferric chloride. The hydrate dissolves in considerable quantity, and a deep red solution is formed, containing from 5 to 6 or 7 molecules of ferric oxide to 1 molecule of the chloride. The solutions may be heated or diluted with water without decomposing; those which contain the larger quantities of oxide deposit a portion of it, however, on the addition of certain salts, and when evaporated, leave residues which do not redissolve in water. Compounds containing not more than 5 at. Fe^4O^3 to 1 at. Fe^2Cl^6 are, on the contrary, perfectly soluble in water after evaporation. (Phillips, Phil. Mag. [3] viii. 406; Ordway, Sill. Am. J. [2] xxvi. 197; Bechamp, Ann. Ch. Phys. [3] lvi. 306; lvii. 296.)

Ferric chloride forms with *chloride of cyanogen*, the compound $Fe^2Cl^6.CyCl$, already described (ii. 279). It unites directly with *pentachloride of phosphorus*, forming the compound $Fe^2Cl^6.PCl^5$, also produced by the action of pentachloride of phosphorus or ferric oxide. It is a brown substance, which melts easily, but is difficult to volatilise. (Weber, Pogg. Ann. cvii. 375.)

Ferric chloride unites with the chlorides of the alkali-metals, forming double chlorides: among which the ammonium salts are the most stable.

Ferrico-ammonic chloride, $2NH^4Cl.Fe^2Cl^6.H^2O$.—A solution of sal-ammoniac in a large excess of ferric chloride, when evaporated over oil of vitriol within a receiver containing air, yields garnet-coloured monoclinic crystals, which may easily be mistaken for regular octahedrons; they are not decomposed by water, like the corresponding compound of chloride of potassium (Fritzsche, J. pr. Chem. xviii. 484). By slowly evaporating a mixture of this nature, L. Gmelin obtained very deliquescent rectangular octahedrons, having two of the basal edges and four of the basal summits truncated.

A solution of from 3 to 24 pts. of sal-ammoniac and 1 pt. of ferric chloride in water, yields, on evaporation, roseate transparent crystals, which, according to Geiger, are acute rhombohedrons when they contain a medium quantity of iron, but obtuse when the proportion of iron is either very small or very large; according to Marx also (Schw. J. liv. 304) they appear to be made up of a very great number of small cubes not quite regularly grouped together, whereby the cubical shape is somewhat altered. The quantity of iron is small and variable. If 24 pts. of sal-ammoniac are used to 1 pt. of the ferric chloride, the crystals contain 0·85 per cent. of ferric chloride; if 14 pts. of sal-ammoniac are used, they contain 1·93; and with 3 sal-ammoniac, they contain 5·12 per cent. of ferric chloride. The mother-liquor of the last-mentioned crystals yields, on further evaporation, brown-red crystalline granules, containing 5·75 per cent. of ferric chloride (Geiger). When 10 pts. sal-ammoniac have been used with 1 pt. ferric chloride, the crystals contain 0·86 per cent of the latter (Winckler, Repert. Pharm. lxvii. 155). The crystals, when heated, become yellow and opaque, and evolve, first sal-ammoniac, and afterwards ferric chloride. They dissolve in 3 pts. of cold water; those in which the proportion of ferric chloride does not exceed 5·12 per cent., become moist only in damp air; those which contain 5·75 per cent. Fe^2Cl^6, become moist even in dry air (Geiger, Repert. xiii. 422). When their aqueous solution is evoporated, sal-ammoniac crystallises out, nearly pure at first, but afterwards continually richer in iron, being first yellow and then red, and there remains a mother-liquid richer in iron.

To these mixtures of ferric chloride and sal-ammoniac belong the *Ferruginous Flowers of Sal-ammoniac, Flores Salis-ammoniaci martiales.* These are obtained:—1. By subliming 16 pts. sal-ammoniac with 1 pt. ferric oxide, whereupon ammonia is evolved: or with 1 pt. iron filings, in which case hydrogen is set free and protochloride of iron and ammonium is produced; the latter, however, if the air has moderately free access to it, is converted into ferrico-ammonic chloride, while ferric oxide is left behind.—2. By subliming a mixture (obtained by evaporation) of 12 pts. sal-ammoniac, and ferric chloride prepared from 1 pt. of iron filings.—3. By dissolving 16 pts. sal-ammoniac and 1 pt. ferric chloride in water, and evaporating to dryness. Some pharmacopœias, however, direct the preparation of the crystals above described. The product is a yellow saline mass, which is yellower and more deliquescent in proportion as it is richer in iron.

Ammonio-sesquichloride of Iron, $NH^3.Fe^2Cl^6$, or *Chloride of Ferricum and Ferric-ammonium*, $NH^3feCl.2feCl$.—Ferric-chloride slowly absorbs ammonia gas at common temperatures, with slight evolution of heat, but without alteration of external appearance. Part of the compound volatilises undecomposed when heated; the rest leaves ferrous chloride. It deliquesces in the air, but not so quickly as pure ferric chloride. When thrown into water in considerable quantities, it dissolves with a hissing noise, and forms a dark red transparent solution. (H. Rose, Pogg. Ann. xxiv. 302.)

Ferrico-potassic Chloride, $2KCl.Fe^2Cl^3.H^2O$.—A solution of chloride of potassium in excess of ferric hydrochlorate evaporated under a bell-jar over oil of vitriol, yields small yellowish-red monoclinic crystals. A small quantity of water extracts chloride of iron from them, and leaves crystals of chloride of potassium undissolved, as may be seen by examination with the microscope. A larger quantity of water dissolves the whole; but, on evaporation, colourless crystals of chloride of potassium separate out first, and afterwards coloured crystals of the ferrico-potassic chloride; and at this degree of concentration, the crystals of chloride of potassium redissolve without any warming or stirring, and are reconverted into crystals of ferrico-potassic chloride. (Fritzsche, J. pr. Chem. xviii. 483.)

Ferrico-sodic Chloride melts at 200°, forming a very mobile liquid. (Deville.)

Ferrico-ammonio-potassio-sodic Chloride—$2(NH^4;K;Na)Cl.Fe^2Cl^3.H^2O$ (containing 12·1 per cent. potassium to 6·2 ammonium and 0·16 sodium)—is found, together with sublimed ferric chloride, in the craters of volcanos, and remains, after the removal of the ferric chloride by deliquescence, in ruby-red regular octahedrons, which may be dried over oil of vitriol. It is very deliquescent, and difficult to recrystallise without decomposition. (Kremers, Pogg. Ann. lxxxiv. 79.)

IRON, CYANIDES OF. (See CYANIDES, ii. 221.)

IRON, DETECTION AND ESTIMATION OF.—1. *Blow-pipe reactions.*—Iron-salts fused in small quantity, with borax on platinum wire in the outer flame, colour the bead yellow while hot, the colour disappearing on cooling. With a larger proportion of iron, the bead is red while hot, and yellow after cooling. In the inner flame a bottle-green glass is produced. With phosphorus-salt, when a moderate quantity of iron-salt is added, the bead is reddish-yellow in the outer flame while hot, becoming yellow as it cools, then green, and finally colourless. With a large proportion of iron, the bead is deep red while hot, becoming red-brown and dirty green as it cools, and reddish-brown when quite cold. The colours change by cooling much more quickly than those of the borax bead. These reactions are common to ferrous and ferric compounds (H. Rose). Ferrous oxide in minerals may be specially distinguished by heating the substance for a very short time in the inner flame with a bead of borax coloured pale blue by a small quantity of oxide of copper; the ferrous oxide then reduces the cupric oxide to cuprous oxide or metallic copper, which forms red spots on the bead. The heat must not be too long continued, as in that case ferric oxide, if present, would be reduced to ferrous oxide, which would then produce the reaction just mentioned. To check this result, a portion of the substance may be heated for a moment in the oxidising flame with a new borax bead containing copper; the bead will then assume a pale green colour if ferric oxide is present, whereas ferrous oxide would produce the red spots in this case also. (Chapman.)

2. *Reactions in Solution.*

Some compounds of iron are soluble in water, and the greater number are soluble in acids; many, however, especially native ferric oxide, and the artificially prepared oxide, after strong ignition, require prolonged boiling with strong hydrochloric acid to dissolve them. The solution of many iron ores, and of ferric oxide in a state of very dense aggregation, may be facilitated by addition of zinc or stannous chloride, which reduces the ferric to ferrous oxide. Many iron ores can be rendered soluble only by fusing them with alkaline carbonates; some only by fusion with acid sulphate of potassium or sodium.

Iron usually exists in solution as a ferric or ferrous salt, or partly in one state, partly in the other; rarely as ferric acid, on account of the great instability of the salts of that acid.

Ferric salts in solution are mostly yellow or reddish-yellow, more rarely (as in the case of the iron-alums) colourless or pale violet. *Sulphydric acid gas* passed into the neutral or acid solution of a ferric salt reduces it to a ferrous salt, with precipitation of sulphur, thus:

$$2Fe^2Cl^3 + H^2S = 2HCl + 4FeCl + S.$$

In a solution of neutral or basic ferric acetate, however, sulphydric acid forms a black precipitate of sulphide of iron; if, on the other hand, the liquid contains free acetic acid, nothing but a milky precipitate of sulphur is produced.

Sulphydrate of ammonium produces, in neutral solutions of ferric salts, a black precipitate of sulphide of iron insoluble in excess of the precipitant, and becoming red-brown by oxidation in contact with the air. If the quantity of iron present is very minute, no precipitate is formed at first, but the liquid acquires a green colour, and if kept for some time in a closed vessel, deposits sulphide of iron in black flocks.

Alkalis and *alkaline carbonates* produce a red-brown precipitate of ferric hydrate insoluble in excess of either of these reagents.

The *carbonates of barium, strontium*, and *calcium*, shaken up with a ferric solution, likewise form a precipitate of ferric hydrate.

Phosphate of sodium forms a white precipitate of ferric phosphate, which is turned red-brown by alkalis, dissolves easily in nitric or hydrochloric acid, but is insoluble in acetic acid.

Ferrocyanide of potassium forms a deep blue precipitate of Prussian blue, insoluble in acids, but dissolving in alkalis, with separation of ferric oxide. If the quantity of iron present is very small, the precipitate appears green, or the liquid merely acquires a green colour, and deposits blue flocks on standing.

Ferricyanide of potassium forms no precipitate, but changes the colour of the liquid to greenish-brown. If the least trace of a ferrous salt is present, a blue precipitate is produced.

Sulphocyanate of potassium changes the colour of ferric salts to deep blood-red, the coloration being very decided even in extremely dilute solutions: this is, in fact, the most delicate of all tests for the presence of iron in the ferric state. The red colour is not modified by addition of a small quantity of hydrochloric acid; but a large quantity nearly destroys it. A certain quantity of nitric acid destroys it completely after a while, and it is not restored by subsequent addition of the ferric salt. The red colour is also destroyed by oxalic, iodic, phosphoric, and arsenic acids, but reappears on again adding a solution of a ferric salt. Ammonia instantly decolorises the red solution and precipitates ferric hydrate. Sulphide of ammonium forms a black precipitate of ferric sulphide.

Infusion of galls colours ferric solutions deep blue-black, and renders them turbid. The precipitate is dissolved and the colour destroyed by free acids.

Ferric salts are easily reduced to ferrous salts by various *de-oxidising agents*; as by sulphydric acid, as already mentioned; by sulphurous, hyposulphurous, and phosphorous acids; by stannous chloride; by metallic iron, and even by silver at the boiling heat.

The reactions with sulphide of ammonium, alkalis, ferro- or ferri-cyanide of potassium, and sulphocyanate of potassium, serve to distinguish ferric salts from all other metallic salts.

Solutions of ferrous salts have a bluish-green or bluish colour, and, when exposed to the air, take up oxygen and are converted wholly or partially into ferric salts; and unless a sufficient excess of acid is present to form a neutral ferric salt with the quantity of iron present, part of the iron is precipitated in the form of a yellow-brown basic salt. They are likewise converted into ferric salts by *aërated water*, by *hypochlorous acid, nitric acid*, and by easily reducible metallic oxides and salts, such as those of *silver, gold*, and *mercury*. When nitric acid is the oxidising agent, the nitric oxide separated from it does not escape from the liquid at ordinary temperatures, so long as any portion of ferrous salt remains unoxidised, but remains dissolved, forming a dark greenish-brown solution.

A concentrated solution of ferrous sulphate or chloride placed in the circuit of a powerful voltaic battery, deposits metallic iron in small granules on the negative platinum wire. If the positive wire is dipped into a solution of common salt separated from the iron solution by moist clay, the iron is obtained in glittering crystals which exhibit magnetic polarity (Becquerel). *Zinc* immersed in a perfectly neutral solution of ferrous sulphate or chloride contained in a stoppered bottle, throws down metallic iron (together with oxide) which is deposited partly on the zinc, partly on the contiguous side of the glass. (Fischer, Pogg. Ann. ix. 266.)

Sulphydric acid forms no precipitate in a solution of ferrous salt containing an excess of one of the stronger mineral acids, but from a solution containing only a weaker acid, such as carbonic, oxalic, tartaric, or acetic acid, it precipitates part of the iron, in the form of a black hydrated ferrous sulphide, the precipitation in the three last-mentioned salts going on only till a moderate portion of acid is set free; the same reagent precipitates ferrous benzoate, and even, to a slight extent, the sulphate and chloride, if the acids are completely saturated with base. From the sulphate or chloride mixed with acetate of potassium, it throws down a considerable portion of the iron, but not the whole, even when the acetate is in excess. The black precipitate acquires a rusty brown colour by exposure to the air. It dissolves readily in hydrochloric or sulphuric acid, and likewise in a large quantity of acetic acid, provided it does not contain excess of sulphur.—The same precipitate, but containing the whole of the iron, is produced in all ferrous salts, on the addition of an alkaline *sulphydrate*, and it is not soluble in an excess of the reagent. A very dilute iron-solution to which sulphydrate of ammonium is added, assumes a green colour, from the presence of iron-sulphide in a state of suspension.

Fixed caustic alkalis completely precipitate the iron in the form of a white hydrate, which, by exposure to the air, acquires a dingy-green and afterwards a red-brown colour.—*Ammonia* throws down part of the iron in the form of hydrate, the rest remaining dissolved in the liquid, which, when exposed to the air, becomes covered, first with a green and afterwards with a brown film. If the ferrous salt is previously mixed with sal-ammoniac, ammonia yields no precipitate, but forms a pale-green mixture which exhibits similar appearances on exposure to the air.

Monocarbonate of potassium or *sodium*, and *sesquicarbonate of ammonium*, throw down white ferrous carbonate, which soon acquires a green and afterwards a brown colour by exposure to the air, and, if sal-ammoniac be added, dissolves in the liquid, which then exhibits a green, and subsequently a brown turbidity on exposure to the air. *Acid carbonate of potassium* or *sodium* forms the same precipitate, with evolution of carbonic anhydride; but, if the solutions are dilute, a clear mixture is formed, which deposits ferrous carbonate on boiling, and on exposure to the air yields a precipitate of ferroso-ferric hydrate.—The *carbonates* of *alkaline earth-metals* do not precipitate ferrous salts. (Fuchs.)

Phosphate of sodium precipitates white ferrous phosphate, which acquires a bluish-green colour by exposure to the air.—*Arsenate of sodium* precipitates white ferrous arsenate, which becomes dingy-green on exposure to the air.

Oxalic acid and *acid oxalate of potassium* communicate a yellow colour to ferrous salts, and, after a while, throw down yellow ferrous oxalate, the precipitation being immediate when an alkaline oxalate is used.

Ferrocyanide of potassium forms a precipitate which is white, if the solution has been perfectly freed from air by boiling and the iron-salt is absolutely free from ferric oxide, but otherwise bluish-white: by exposure to the air, this precipitate is converted into Prussian-blue. *Ferricyanide of potassium* gives a deep blue precipitate (ii. 244), even in very dilute solutions.

Sulphocyanate of potassium neither alters the colour of ferrous solutions, nor forms any precipitate in them.

Tincture of galls neither colours nor precipitates ferrous salts when they are quite free from ferric oxide; but the mixture acquires a violet-black colour on exposure to the air.

The preceding reactions, especially those with the alkalis, and with ferrocyanide, ferricyanide, and sulphocyanate of potassium, afford marked distinctions between ferrous and ferric salts; it is but rarely, however, that ferrous solutions can be obtained so pure as to give the reactions exactly as they are above described, exposure to the air for a very short time being sufficient to convert a portion of the ferrous into ferric salt: hence the precipitate formed by ferrocyanide of potassium is generally somewhat bluish, and those formed by the alkalis have more or less of a dark-green tinge. The best way of obtaining a solution of iron quite free from ferric salt, is to immerse a few pieces of bright iron wire in aqueous sulphurous acid: a mixture of ferrous sulphite and hyposulphite is then formed, which gives a perfectly white precipitate with ferrocyanide of potassium.

Solutions containing both ferrous and ferric salts, such as are obtained by dissolving magnetic oxide of iron in hydrochloric acid, of course give reactions intermediate between those of pure ferrous and pure ferric salts; in particular, they give blue precipitates both with ferrocyanide and with ferricyanide of potassium; the formation of both these precipitates in a solution obtained by dissolving a mineral in hydrochloric or sulphuric acid, without the addition of any oxidising agent, such as nitric acid, may be taken as an indication that the mineral contains a mixture or compound of ferrous and ferric oxides. From such mixed solutions, the ferric oxide may be precipitated by means of carbonate of barium, while the ferrous oxide will remain in solution.

For the reactions of iron in the state of ferric acid, see ii. 637.

3. *Quantitative Estimation of Iron.*

Iron is always estimated by weight in the form of ferric oxide. If the solution contains ferrous oxide, either alone or mixed with ferric oxide, it is first boiled with a sufficient quantity of nitric acid to convert the whole of the ferrous oxide into ferric oxide, and then treated with *ammonia* in excess to precipitate the latter. The precipitate is collected on a filter, washed, dried, and ignited at a moderate red heat; too high a temperature expels a portion of the oxygen. Every 10 pts. of pure ferric oxide correspond to 7 pts. of metallic iron. In some cases, however, it is necessary to use *potash* as the precipitant. In that case, the precipitated ferric oxide is very apt to carry down with it a portion of the potash, which is exceedingly difficult to remove by washing. It is best therefore, after having washed it two or three times with hot water, to redissolve it in acid and precipitate by ammonia. In other cases, as when the solution contains organic matter, the iron must be precipitated by *sulphide of ammonium*, because such substances prevent the precipitation of the oxide. To ensure complete precipitation, the liquid, after being mixed with excess of sulphide of ammonium, should be left for some time in a covered vessel standing in a warm place till it becomes quite colourless or yellow, then filtered as quickly as possible, protecting it from the air, and the precipitate washed with water containing sulphide of ammonium. The precipitated sulphide is then dissolved in nitric acid, and the iron precipitated by ammonia as before.

If the iron is mixed or combined merely with volatile or with easily combustible substances, its amount may be determined by simple ignition in contact with the air; all the volatile and combustible matters will then be driven off or burnt away, and the iron will be left in the form of ferric oxide: to ensure its complete conversion into this oxide, however, the residue should be moistened with nitric acid, and heated again.

An indirect method of estimating iron, given by **Fuchs** (J. pr. Chem. xvii. 160), depends upon the fact that metallic *copper* does not dissolve (or dissolves but very slowly, and only when finely divided, ii. 40) in hydrochloric acid, if kept from contact with the air, but when boiled with ferric chloride, it dissolves, with formation of ferrous and cuprous chlorides:

$$Fe^2Cl^3 + Cu^2 = 2FeCl + Cu^2Cl.$$

The solution of ferric chloride mixed with excess of dilute hydrochloric acid and diluted with water, is boiled in a flask, and clean copper-foil, not too thin (from 15 to 20 pts. copper to 2 or 3 pts. ferric oxide), is completely immersed in the liquid; the flask is closed with a perforated cork, having a narrow glass tube passing through it, and the liquid is boiled till it becomes permanently bluish-green or colourless. It is then left to cool with the flask closed; decanted from the undissolved copper; this copper washed by repeated affusion with hot water, and decantation, then dried between bibulous paper, and finally by heat, taking care not to rub it, and weighed. The loss of weight multiplied by 0·894 gives the quantity of iron in the solution: for each atom of copper (= 31·5) represents 1 at. iron (= 28) in the solution, and $\frac{28}{31\cdot5} = 0\cdot894$. Or the loss of weight multiplied by $\frac{80}{63\cdot5} = 1\cdot252$ will give the quantity of ferric oxide in the solution. To ensure the complete reduction of the ferric to ferrous chloride, it is essential that the air be entirely excluded from the vessel, and therefore that the boiling be kept up uninterruptedly till the liquid has become colourless.

Silver in the spongy state may also be used to reduce the ferric chloride. The products of the reaction are ferrous chloride, which remains in solution, and chloride of silver, which mixes with the metallic silver, and increases its weight. As in this reaction, each atom of chlorine that enters into combination with the silver corresponds to 2 at. iron ($Fe^2Cl^3 + Ag = 2FeCl + AgCl$), the increase of weight multiplied by $\frac{2 \times 28}{35\cdot5} = 1\cdot5774$ gives the quantity of iron in the solution; or $\frac{80}{35\cdot5} = 2\cdot2535$ gives the quantity of ferric oxide.

The method of reduction by copper or silver may be applied to determine the quantities of ferrous and ferric oxides, when they exist together in solution. The quantity of ferric oxide, or of iron existing as ferric salt, is first determined as above, the ferrous salt present not interfering with the reaction. It is necessary, however, to guard against the conversion of the ferrous into ferric salt by atmospheric oxidation: for which purpose it is best to perform the determination in an atmosphere of nitrogen or carbonic anhydride. Another portion of the solution is then treated with chlorine to convert the ferrous salt contained in it into ferric salt, and in this solution the total quantity of iron is determined by the same method. The difference of the two determinations gives the quantity of iron existing as ferrous salt.

Ferrous and ferric oxides may likewise be separated by means of *carbonate of barium* or *carbonate of calcium*, which precipitates ferric oxide from slightly acid solutions, but not ferrous oxide. It is necessary to have the solution slightly acid, since if it is perfectly neutral, a small quantity of ferrous oxide may likewise be precipitated. The solution, which should be slightly warmed, is shaken up with recently precipitated carbonate of barium (which acts more quickly than carbonate of calcium), in a corked flask filled with carbonic anhydride; then left to stand, and shaken up again from time to time, till it has become quite colourless, afterwards filtered, and the precipitate washed, always in an atmosphere of carbonic anhydride. The precipitate, consisting of carbonate of barium mixed with ferric hydrate, is dissolved in dilute hydrochloric acid, the baryta precipitated by sulphuric acid, and the ferric oxide from the filtrate by ammonia. This determines the quantity of iron existing in the solution as *ferricum*. To find the quantity existing as *ferrosum*, the liquid filtered from the precipitate of carbonate of barium and ferric oxide is boiled with nitric acid, to convert the ferrous into ferric salts, then freed from baryta by sulphuric acid, and the iron is precipitated as ferric oxide by treating the filtrate with ammonia. Or another portion of the original solution may be treated with nitric acid, to bring all the iron into the ferric state, and the total quantity of iron determined by precipitation with ammonia. The difference of the two determinations will then give the quantity of iron existing as ferrosum.

Anhydrous ferroso-ferric oxides may be analysed by dissolving them in nitric or nitromuriatic acid, and precipitating the iron as ferric oxide by ammonia. The proportions of iron and oxygen are thus determined, whence the formula may be calculated.

Volumetric estimation of iron.—When iron is contained in a solution as ferrous oxide or ferrous salt, it may be estimated by determining the quantity of an oxidising agent required to convert it into ferric oxide; if, on the other hand, it is present as ferric oxide, the estimation may be made by measuring the quantity of a reducing agent required to bring it to the state of ferrous oxide.

1. *Methods depending on oxidation.*—The reagent most generally employed for converting ferrous into ferric oxide in volumetric analysis is *permanganate of potassium*. The method of applying it is fully described in the article ANALYSIS, VOLUMETRIC (i. 263).—If the iron in the solution under examination is present wholly as ferrosum, the method is directly applicable; if, on the contrary, the iron is present wholly or partly as ferricum, it must first be brought to the ferrous state by heating it with sulphurous acid or sulphite of sodium, or better with a few grains of pure zinc. In a mixture of ferrous and ferric salts, the ferrosum may be determined by treating one portion with the permanganate directly, and another after reduction of the ferric salt in the manner just described.

Acid chromate of potassium may also be used for the volumetric estimation of iron, and has the advantage of not varying in strength when its solution is kept in well closed vessels. The reaction between ferrous oxide and chromic acid may be represented by the equation:

$$\underset{\substack{\text{Chromic}\\\text{anhydride.}}}{2Cr^2O^3} + 6Fe^2O = 3Fe^4O^3 + \underset{\substack{\text{Chromic}\\\text{oxide.}}}{Cr^4O^3}$$

whence we find that 1 grm. of iron requires 0·8849 grms. of acid chromate of potassium, $K^2O.2Cr^2O^3$, to convert it from ferrous into ferric oxide. If, then, 8·849 grms. of the pure acid chromate are made into a litre (1000 cub. cent.) of solution, 100 cub. cent. of this solution will correspond to exactly 1 grm. of iron. The solution of the acid chromate is slowly added to the acid ferrous solution till a drop of the liquid no longer forms a blue precipitate with red prussiate. (Penny, Chem. Gaz. 1850, p. 599.)

Bunsen (Ann. Ch. Pharm. lxxxvi. 288) adds to the ferrous solution mixed with hydrochloric acid, a weighed quantity of acid chromate, more than sufficient for the complete oxidation of the ferrous salt, passes the chlorine evolved on heating, into a solution of iodide of potassium, and estimates the quantity of iodine thus liberated by the method described under ANALYSIS, VOLUMETRIC (i. 265). If no ferrous oxide were present, 1 at. $K^2O.2Cr^2O^3$ would give 3 at. chlorine, and therefore 3 at. iodine; but as a portion of the chlorine is used up in converting the ferrous into a ferric salt, there will be 1 at. less of iodine set free for every 2 at. iron present as ferrosum. The quantity of iron x will therefore be given by the formula:

$$x = \frac{6Fe}{K^2O.2Cr^2O^3} \cdot p - \frac{2F}{I}\, a\,(nt - t')$$

where p denotes the weight of acid chromate used, and a, n, t, t' have the same significations as in the article just cited.

For the exact estimation of iron in cast iron, iron ores, &c., Mohr uses two titrated solutions, one containing 8·785 grms. of the acid chromate in a litre, therefore 1 cub. cent. = 0·01 grm. iron; the second diluted ten times as much, therefore 1 cub. cent. = 0·001 grm. iron. A quantity of the substance, containing about 1 grm. of pure iron (that is to say 1·05 grm. pig iron, or 2·00 grms. iron ore, supposing the latter to contain about 50 per cent. iron) is then weighed out, and dissolved in hydrochloric acid; the whole of the iron in solution is brought to the ferrous state by reduction with zinc, &c.; the solution is then mixed with 100 cub. cent. of the stronger solution of chromate and the more dilute solution is afterwards added from a burette, till the liquid no longer gives a blue colour with ferricyanide of potassium.

Or 1 grm. of the carburetted iron is dissolved in acid, &c.; the solution is mixed with 100 cub. cent. of the stronger chromate-solution; and as an excess of the latter is then present, it is titrated backwards with a graduated acid solution of ferroso-ammonic sulphate (1 litre of this solution containing 7000 grms. of the crystallised salt $(NH^4)FeSO^4.3H^2O$, together with a small quantity of free sulphuric acid, so that 1 cub. cent. = 0·001 grm. iron), till a blue colour is produced on addition of ferricyanide of potassium. The number of cubic centimetres of this iron-solution used must of course be deducted, as so many milligrammes of iron. (**Mohr**, Dingl. pol. J. clix. 124.)

2. *Methods depending on Reduction.*—**Streng** (Pogg. Ann. xciv. 493) dissolves the metal or ore to be valued in boiling hydrochloric acid; oxidises, if necessary, with chlorate of potassium; dilutes with cold water, after expelling the free chlorine, and mixes the solution with excess of iodide of potassium, whereby iodine is set free:

$$Fe^2Cl^3 + 3KI = 2FeI + 3KCl + I.$$

A dilute titrated solution of *stannous chloride* is then added—whereby the brown colour of the solution is rendered lighter—and when only a small quantity of iodine remains in the free state, some clear starch-solution; then more stannous chloride, by drops, till the blue colour disappears. If the tin-solution has been titrated with acid chromate of potassium, the percentage of metallic iron is given by the formula:

$$x = \frac{100 . 12Fe . c}{A.(K^2O.2Cr^2O^3)} . \frac{CG}{g},$$

where c denotes the quantity of acid chromate in 1 c.c. of the standard solution of that salt, G the number of cubic centimetres of tin-solution added to produce decoloration, g the number of cubic centimetres of the same tin-solution used in determining its strength, C the number of cubic centimetres of the chrome-solution used to oxidise the g cub. cent. of tin-solution, and A the quantity of iron or ore dissolved.

Mohr (Ann. Ch. Pharm. cxiii. 257) after bringing the whole of the iron to the state of ferric chloride (by treating the solution of ferrous chloride with artificially prepared peroxide of manganese, and boiling to expel free chlorine), adds a small quantity of sulphocyanate of potassium, and then a standard solution of *stannous chloride*, till the red colour disappears, the tin-solution having been previously titrated with a solution of pure ferric chloride. Or the solution of ferric chloride under examination is mixed with starch and iodide of potassium heated to 50° or 60°, and the standard tin-solution added till the colour disappears. **Fresenius** uses a solution of stannous chloride of such a strength, that from 50 to 100 c.c. are required to reduce 1 grm. of pure iron (1·003 grm. harpsichord-wire) from ferric to ferrous chloride. He dissolves the iron or iron-compound in hydrochloric acid, oxidises with chlorate of potassium, and adds to the slowly but continuously boiling liquid, after all the free chlorine has been expelled, a quantity of standard tin-solution rather more than sufficient to decolorise it. The cooled liquid is then mixed with starch-solution; and a solution of iodine and iodide of potassium (containing about 0·005 grm. iodine in a litre), previously titrated against the tin-solution, is added till a permanent blue colour is produced. The quantity of this iodine-solution required for the purpose gives the *excess* of tin-solution previously added.

In using a solution of stannous chloride for the estimation of iron, it is essential that the water with which the iron-solution is diluted be free from air; otherwise a portion of the stannous salt will be oxidised thereby.

When ferric chloride is brought in contact with *hyposulphite of sodium*, tetrathionate of sodium is formed, together with chloride of sodium and ferrous chloride, but no sulphuric acid:

$$2Fe^2Cl^3 + \underset{\text{Hyposulphite of sodium.}}{2Na^2S^2O^3} = 4FeCl + 2NaCl + \underset{\text{Tetrathionate of sodium.}}{Na^2S^4O^6}.$$

According to this equation, 248 parts crystallised hyposulphite of sodium $(Na^2S^2O^3.5H^2O)$ correspond with 162·5 pts. ferric chloride; or 100 pts. iron, present as ferricum, require for reduction to ferrosum, 442·9 pts. of the crystallised hyposulphite.

Mohr (*loc. cit.*) uses hyposulphite of sodium in the same way as stannous chloride, mixing the solution of ferric chloride with iodide of potassium, a little hydrochloric acid and starch-paste, heating it to 50°–60°, and adding the standard solution of hyposulphite till the blue colour disappears.

These reduction-processes may also be used for determining the proportions of ferric and ferrous salt existing in the same solution, one portion of the solution being titrated in its original state, another after all the iron has been converted into ferric salt; the difference gives the amount of iron existing as ferrous salt.

4. *Separation of iron from other elements.*

From all metals of the first group (i. 217), iron is easily separated by *sulphydric acid*, which throws down all those metals, leaving the iron in solution. The filtrate, which contains the iron in the form of ferrous salt, must then be heated with nitric acid to oxidise the iron, which may afterwards be precipitated by ammonia.

The separation of iron from the metals of the second group, which are not precipitated by sulphydric acid from acid solutions, but are precipitated, together with iron, by sulphide of ammonium from neutral or alkaline solutions, is more difficult.

From manganese (present as manganous salt) and from zinc, iron is most effectually separated by *succinate* or *benzoate of ammonium.* The solution, after all the iron has been brought to the state of ferric salt, is mixed with a sufficient quantity of sal-ammoniac to hold the manganese or zinc in solution, and very carefully neutralised with ammonia; it is then treated with benzoate or succinate of ammonium, which throws down the iron as ferric benzoate or succinate, leaving the manganese or zinc in solution. The precipitate is washed, dried, and ignited in an open platinum crucible, so that the air may have sufficient access to it, to prevent any reduction of the iron by the carbon of the organic acid. Should such reduction take place, the iron must be reoxidised by nitric acid. The success of this mode of separation depends entirely on the care with which the acid in the solution is neutralised with ammonia before adding the benzoate or succinate. If too much ammonia has been added, manganese or zinc goes down with the iron; if too little, a portion of iron remains in solution. The addition of ammonia should be continued till a small quantity of ferric oxide is precipitated, and does not redissolve on agitation. The supernatant liquid has then a deep brown colour, the greater part of the iron being still in the solution.

The separation of iron (as *ferricum*) from manganese and zinc may also be effected by agitating the solution with *carbonate of barium* (as in the separation of ferric from ferrous oxide, p. 383), which precipitates the iron as ferric oxide, leaving the other metals in solution.

According to J. Schiel (Sill. Am. J. [2] xv. 275) manganese may be separated from iron by mixing the solution with *acetate of sodium*, and passing *chlorine* through it, which throws down the manganese as peroxide.

Zinc may be separated from iron (ferricum) when both are present as acetates in a solution containing a sufficient quantity of free acetic, but no inorganic acid, by passing *sulphydric acid gas* through the solution, the zinc being then precipitated while the iron remains in solution. If the two metals are combined with any other acid, they must be precipitated by carbonate of potassium, and redissolved in acetic acid; or if they are present as sulphates, they may be converted into acetates by decomposition with acetate of barium.

For the methods of separating iron from cobalt, see vol. i. p. 1046. When the two metals are precipitated together by sulphide of ammonium, the separation may be effected by digesting the sulphides with acetic, as well as with dilute hydrochloric acid; the iron then dissolves as acetate, while the cobalt remains behind.

Iron may be separated from nickel by the same methods as from cobalt (excepting that with nitrite of potassium). Nickel may also be separated from iron (*ferricum*) by mixing the solution with a large quantity of sal-ammoniac (20 pts. of that salt to 1 pt. of nickel), precipitating the iron with *carbonate of ammonium*, then heating the liquid slowly to the boiling point, keeping it at that temperature for some time, adding a small quantity of ammonia and filtering: ferric oxide then remains on the filter, while all the nickel passes through in solution (Schwarzenberg, Ann. Ch. Pharm. xcvii. 216). Iron and nickel may also be separated by precipitating the iron as ferric oxide with *carbonate of barium.* For the separation of iron from cobalt, this method is not so well adapted, because a small portion of the cobalt is apt to be precipitated at the same time.

Uranium may be separated from iron, both being in the state of sesquioxides, by treating the solution with excess of *carbonate of ammonium*, which precipitates the ferric oxide, and retains the uranium in solution. The carbonate of ammonium must, however, be quite neutral, as if it contains any excess of carbonic acid, part of the iron may be redissolved. To ensure this condition, the carbonate of ammonium should be previously boiled, and the solution of the metals, if acid, must be neutralised with ammonia till a slight permanent precipitate begins to form; the solution is then to be diluted with water, the carbonate of ammonium added, and the precipitate digested with it for some time before filtering.

For the separation of iron from cerium, chromium, didymium, lanthanum, molybdenum, niobium, platinum and its congeners, tantalum, titanium, tungsten, and vanadium, see those metals; also pp. 374, 375.

From **aluminium**, iron in the form of ferric salt may be separated by caustic potash, which when added in excess, and boiled with the concentrated solution of the two salts, precipitates the iron as ferric oxide, and retains the alumina in solution. If the proportion of iron is small (not exceeding 1 pt. ferric oxide to 100 alumina), this method of separation is sufficiently exact; but when it is larger, a portion of the alumina always remains with the ferric oxide, and must be separated by redissolving the precipitate in a small quantity of hydrochloric acid, and repeating the treatment with potash. With very large quantities of iron, this treatment must sometimes be repeated three or four times before complete separation is effected. The process may be modified by first reducing the ferric solution with sulphurous acid or an alkaline sulphite, and then boiling with potash till the iron is precipitated as dark green ferroso-ferric oxide; but in this way also the separation is not quite complete; if too much sulphurous acid is added, a small quantity of sulphite of aluminium is sometimes precipitated on boiling.

Iron and aluminium may, however, be much more easily separated by means of *hyposulphite of sodium*, which precipitates alumina together with sulphur, leaving the iron in solution (i. 155).

Another very good method of separating iron and aluminium is to mix the solution with a quantity of *tartaric acid*, sufficient to prevent the precipitation of the oxides when the liquid is rendered alkaline, then add excess of ammonia, and precipitate the iron as sulphide by *sulphide of ammonium*. The same method serves to separate iron from various other metals, *e.g.* cerium, glucinum, magnesium, thorinum, yttrium, and zirconium.

Aluminium (or glucinum) may also be separated from iron by precipitating the alumina and ferric oxide together with *ammonia*, and igniting a weighed quantity of the washed and calcined precipitate in a stream of hydrogen. The iron is then reduced to the metallic state, while the alumina remains unaltered. The loss of weight gives the quantity of oxygen which was combined with the iron, whence the quantity of ferric oxide may be calculated, and the alumina determined by difference. As a check on the result, which is especially necessary when the quantity of iron is small, the residue may be digested for 24 hours, without heating, in very dilute nitric acid (1 pt. acid of specific gravity 1·2 diluted with more than 30 pts. water), which dissolves the iron without attacking the ignited alumina. A slight loss may arise in this process, in consequence of particles of the alumina (or glucina) being carried over by the stream of hydrogen (Rivot). Deville modifies this process by exposing the mixture of metallic iron and alumina, obtained as above, to a very strong red heat, in a stream of *hydrochloric acid* gas, whereby the iron is volatilised as chloride, while the alumina remains unaltered, and may afterwards be weighed; the iron is then determined by difference. Or the iron may also be directly determined by passing the vapour of boiling hydrochloric acid into the tube and attached receiver, in which the chloride of iron is condensed, oxidising the solution of ferrous chloride thus obtained with nitric acid, and precipitating by ammonia.

From **glucina**, and from most other protoxides, iron in the form of sesquioxide may be separated by precipitation with carbonate of barium (p. 383).

From **magnesia**, ferric oxide may be separated by precipitation with *ammonia* after addition of sal-ammoniac—better with *succinate* or *benzoate of ammonium*, as already described for manganese (p. 386), or with *carbonate of barium*.

From the **alkalis** and **alkaline earths**, ferric oxide may be separated by *ammonia;* in the case of the alkaline earths, however, care must be taken not to add more than a slight excess of ammonia, and to protect the precipitate from the air during filtration and washing; otherwise carbonic acid will be absorbed, and earthy carbonates will be precipitated, together with the ferric oxide, and the precipitate, after washing, will appear light-coloured; it must then be redissolved in acid, and reprecipitated by ammonia. If the solution contains any organic substance, the iron must be precipitated by sulphide of ammonium (p. 383).

Precipitation by ammonia serves to separate iron in the ferric state from most of its inorganic salts, *e.g.* the nitrate, sulphate, &c. From **phosphoric** or **boric acid** it may be separated by dissolving the salt in hydrochloric acid, adding tartaric acid in sufficient quantity to prevent precipitation by alkalis, then adding excess of ammonia, and precipitating the iron by sulphide of ammonium.—For other methods of analysing phosphates of iron, see PHOSPHORIC ACID.

From **arsenic**, iron may be separated by precipitation with *sulphydric acid*, the arsenite or arsenate of iron being dissolved in hydrochloric acid. These salts may also be decomposed in the dry way, by ignition in a stream of sulphydric acid gas, sulphide of arsenic then volatilising, and sulphide of iron remaining. (See also p. 374.)

5. *Assay of Iron ores.*

1. *In the wet way.*—From most ferruginous minerals that are actually used for the extraction of iron, viz. the oxides and carbonates, the iron may be dissolved out by boiling with hydrochloric acid, the insoluble residue consisting of quartz, clay, &c., which may be further analysed by fusion with an alkaline carbonate.

The acid solution generally contains—besides iron—manganese, aluminium, calcium, magnesium, the alkali-metals, and small quantities of sulphur, phosphorus, arsenic, silicium, and titanium, and less frequently copper, zinc, lead, vanadium, chromium, molybdenum, and tungsten. These elements may be detected and separated by methods already described, or to be described, under their respective heads (see also pp. 374—376). The last four, together with titanium, may be separated by fusing the pulverised ore with a mixture of alkaline carbonate and nitrate, and treating the fused mass with water, whereby a solution is formed, which may contain titanate, vanadate, chromate, molybdate, and tungstate of alkali-metal, together with silicate, arsenate, and phosphate.

If the whole of the iron cannot be extracted from an ore by boiling with hydrochloric acid, it must be pulverised and fused with carbonate or acid sulphate of alkali-metal (bisulphate of potash), and the fused mass then dissolved in water or aqueous acid, freed from silica by evaporation, and further examined for the above-mentioned constituents.

In the complete quantitative analysis of iron ores, it is necessary to determine the water and carbonic acid. The water may be estimated by igniting the ore in a glass tube, and condensing the aqueous vapour by means of chloride of calcium; the carbonic acid by the method described under ALKALIMETRY (i. 119). When either water or carbonic acid is present alone, its amount may be determined by the loss of weight sustained on ignition.

If the percentage of iron in the ore is the only point to be determined, the iron, after being brought into the ferric state by oxidation with nitric acid, may be precipitated by ammonia, or, if phosphoric and arsenic acids are present, by sulphide of ammonium after addition of tartaric acid (p. 387). Alumina, if present, must be separated by one of the methods already described. All the trouble of these separations may, however, be avoided by adopting Fuchs' method of estimation with metallic copper, which gives correct results, provided all necessary precautions are taken to exclude the air, or by one of the volumetric methods already described.

2. *In the dry way.*—The object of this mode of assaying, which is an imitation, on the small scale, of the process which goes on in the blast furnace, is to determine, not only the quantity of iron contained in an ore, or rather the quantity that can be extracted by smelting, but likewise the quality of the pig iron obtainable, and generally also that of the slag.

10 grms. of the finely-pounded ore are mixed with 3 to 10 grms. of anhydrous borax (according to the proportion of the gangue); and the mixture is placed in a crucible lined with charcoal (*creuset brasqué*),[*] and exposed in a powerful air-furnace or a portable blast-furnace—Griffin's blast gas-furnace (ii. 787), for example—to a gradually increasing heat, raised at last to whiteness. After cooling, there is found in the crucible, if the operation is successful, a well-fused regulus of cast iron, and above it a slag composed of borax and the materials of the gangue. The regulus must be carefully freed from slag and weighed. It should have a grey colour without much appearance of separated graphite. A large separation of graphite shows that the heat has been too great. If the metal is white, it is very fusible and probably contains manganese; it is then imperfectly carbonised, or it contains phosphorus, arsenic, or sulphur. The slag should not contain either globules of iron mechanically mixed (these, if present, must be separated from the pulverised slag by levigation, or by the magnet), or iron chemically combined, which latter condition will be indicated by a green colour in the slag. The weight of the regulus is increased by the carbon which it contains, but, on the other hand, a small quantity of iron always remains in the slag, and the two errors thus produced may, for the most part, be regarded as compensating one another.

Sometimes powdered glass free from metal is used instead of borax, to increase the fusibility of the gangue; or the ore to be assayed is mixed with the same kind of flux that is to be used in the actual smelting process—that is to say, with chalk, if the gangue consists of quartz or clay, or with clay if the gangue is chiefly limestone. To ascertain approximately the quantity of flux required, a preliminary analysis may be made:—1. By gently igniting 10 grms. of the ore, to determine the amount of water and carbonic acid.—2. By exhausting another sample with very dilute nitric acid, to determine, by the loss of weight after washing and heating, the amount of water, carbonic acid, and lime, taken together.—3. By boiling with hydrochloric acid till all the iron is dissolved out, and weighing the residue, which consists of quartz and clay: the loss of weight in this experiment, compared with that in the second, gives the amount of ferric oxide.

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[*] To prepare these crucibles, a Hessian or Cornish crucible is lined with successive layers of a paste composed of fine charcoal-powder mixed with water, the whole being well stamped with a wooden pestle. As soon as a layer has been well pressed, its surface must be roughened with a knife, so that the next layer may adhere to it well; otherwise the layers will separate when heated. The crucible having been thus filled with stamped charcoal, the portion which projects over the edge is removed, a cavity with rounded bottom is made in the middle, and the sides and bottom of this cavity are polished with a rounded glass rod

These points being determined, 10 grms. of the ore are mixed with such a quantity of clay or chalk that the assay may contain 3 pts. chalk to 2 pts. clay (Regnault). A certain quantity of fluorspar or borax may likewise be added. For rich ores, Karsten takes 1 grm. fluorspar and 1 grm. calcined borax to 10 grms. of ore; for the poorer ores 2·5 grms. fluor and an equal quantity of chalk; and for very poor ores, the same, with 1 grm. borax.

For ores not containing silica, a certain quantity of clay or quartz is added with the fluorspar. Or 10 grms. of ore are mixed with the following proportions of flux:

Magnetic iron ore . . .	1 grm. chalk and	2·5 grms. fluorspar.
Specular iron ore . . .	0·5 „ „	2·5 „ „
Red hæmatite . . .	2·5 „ „	2·5 „ „
Brown hæmatite . . .	2·0 „ „	2·0 „ „
Clay iron ore . . .	2·5 to 3·0 „ „	2·5 to 3·0 „ „
Sparry iron ore . . .	1·0 „ „	2·0 to 3·0 „ „

If the right proportion of flux has been added, and the proper temperature attained, a well-constituted regulus is produced (p. 388), together with a good slag, having a grey-yellowish or sometimes violet colour, an enamel-like or sometimes glassy aspect, and a conchoïdal fracture. If the slag is stony or earthy, yellow, grey, or brown, with rough fracture, it is too rich in bases; too great an excess of lime causes it to crumble easily when touched. If, on the other hand, there is an excess of silica, the slag is glassy, more or less transparent, of green colour (arising from ferrous oxide), and very brittle. The results of a successful assay yield the requisite data for smelting on the large scale.

6. *Atomic Weight of Iron.*

The atomic weight of iron has been determined in several ways:—1. From the weight of ferric oxide obtained by dissolving a known quantity of pure iron (harpsichord wire) in nitric acid, precipitating with ammonia, &c., the small quantity of carbon contained in the iron being estimated and allowed for.—2. From the quantity of iron obtained by reducing a known weight of ferric oxide with hydrogen.—3. By measuring the volume of hydrogen evolved in the solution of iron in hydrochloric acid.—4. From the quantity of chloride of silver obtained by precipitating a known quantity of pure ferrous or ferric chloride with nitrate of silver. The following table exhibits the results obtained by various chemists; the determinations are arranged in chronological order, and the bracketed numbers indicate the method employed:

Berzelius* (1) . . .	Fe = 27·12	Berzelius§ (1) . . .	Fe = 28·03
Gay-Lussac† (1) . . .	Fe = 28·36	Erdmann & Marchand‖ (2)	Fe = 28·01
„ (3) . . .	Fe = 28·27	Maumené¶ (1) . . .	Fe = 27·98 28·02
H. Davy‡ (4) . . .	Fe = 27·98		
Svanberg and Norlin§ (1) .	Fe = 27·94	Dumas** (4) . . .	Fe = 28·10 27·99
„ „ (2) .	Fe = 27·99		

The number 27·12, deduced from the first experiments of Berzelius, was for many years received as the true atomic weight of iron, although Bucholz, some years before, had made a determination of the composition of ferric oxide, which now appears to have been nearer the truth. Berzelius was afterwards led to conclude that his first experiments were affected with an error, arising from the action of the nitric acid on the glass vessel used, and from subsequent experiments, in which platinum vessels were employed, he obtained the higher number 28·03. The whole number 28, which is the mean of all the most trustworthy determinations, is now universally adopted as the true atomic weight of iron, on the supposition that the metal is monatomic in the ferrous, and sesqui-atomic in the ferric salts, *e.g.* ferrous chloride = FeCl; ferric

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[*] Gilb. Ann. vii. 313.

[†] Ann. Chim. lxxx. 163.

[‡] Phil. Trans. cii. 181.

[§] Ann. Ch. Pharm. l. 432.

[‖] Ibid. lii. 212.

[¶] Ann. Ch. Phys. [3] xxx. 380.

[**] Ann. Ch. Pharm. cxiii. 26.

chloride = Fe^2Cl^3. If, however, iron is supposed to be diatomic in the ferrous, and triatomic in the ferric compounds—a view which is more in accordance with recent investigations, *e. g.*

Ferrous chloride . . .	$FfeCl^2$	Ferric chloride . . .	$FfeCl^3$
Ferrous oxide . . .	$FfeO$	Ferric oxide . . .	Ffe^2O^3,

then the atomic weight is Ffe = 56. (See METALS, ATOMIC WEIGHTS OF; also i. 470; ii. 30.)

The equivalent of iron, that is to say, the quantity of the metal which replaces 1 at. of hydrogen, is, in the ferrous compounds, *e. g.* FeCl, equal to 28, and in the ferric compounds, *e.g.* Fe^2Cl^3, or $FeCl^{\frac{2}{3}}$, it is ⅔ of 28, or 18⅔, which number is denoted by fe. (See EQUIVALENTS, ii. 403.)

IRON, FLUORIDES OF. *Ferrous fluoride*, FeF or $FfeF^2$, is obtained by dissolving iron in aqueous hydrofluoric acid, and crystallises by evaporation, or as the solution approaches saturation, in small, colourless, rectangular plates containing water, which they give off without decomposition when moderately heated. The anhydrous fluoride is not altered by ignition, even in contact with the air, but the hydrated salt soon turns yellow on exposure to the air, and if quickly heated, oxidises partially, giving off hydrofluoric acid. The hydrated crystals dissolve slowly in pure water, more easily in acids. Ferrous fluoride forms with *fluoride of potassium* a soluble double salt, KF.FeF, which separates in granular crystals. (Berzelius.)

Ferric fluoride, Fe^2F^3 or $FfeF^3$, is obtained by dissolving ferric oxide or hydrate in aqueous hydrofluoric acid, and separates on evaporation in pale flesh-coloured crystals. When heated in a platinum crucible, over a lamp urged by a blast, it melts, sometimes exhibiting on the surface small cubic crystals of the fluoride, while the fused mass has a rose-red colour, perhaps due to the formation of a small quantity of ferric oxide. Ferric fluoride is isomorphous with fluoride of aluminium, somewhat more fusible than that compound, and equally volatile. (Deville, Compt. rend. xliii. 970.)

Ferric fluoride dissolves slowly but completely in water, forming a colourless, sweetish, astringent liquid. Its solution mixed with ammonia deposits a basic salt, or oxyfluoride, which, when dry, forms a rust-yellow powder.

Mixtures of the solutions of ferric fluoride and fluoride of potassium deposit, on slow cooling, colourless, crystalline, sparingly soluble double salts. If the solution of the ferric fluoride is added by drops to that of the potassic fluoride, the salt formed is $KF.Fe^2F^3$, in the contrary cases, $2KF.Fe^2F^3$. (Berzelius.)

IRON-GLANCE. *Specular Iron ore.* See IRON, OXIDES OF (p. 385); also IRON (p. 338).

IRON, HYDRATES OF. See IRON, OXIDES OF (pp. 393—399).

IRON, HYDRIDE OF. The flame of hydrogen evolved by dissolving iron in dilute acids sometimes yields black spots when a cold piece of porcelain is held in it, and has hence been supposed to contain a gaseous compound of iron and hydrogen; but Fresenius and Schlossberger (Ann. Ch. Pharm. xliv. 264), and other chemists, have shown that these spots are produced by phosphorus, and that the gas, when perfectly freed from mechanical impurities, does not produce them. Cameron (Chem. News, ii. 181) has shown that no ferruretted hydrogen is formed by dissolving the alloy of iron and sodium in acids.

When ferrous iodide is treated with zinc-ethyl and ether, gas is evolved (consisting of hydride of ethyl and hydrogen), and the residue, after washing with ether, yields a hydride of iron, mixed with metallic iron, in the form of a black powder, resembling metallic iron, and decomposing, with evolution of hydrogen, in contact with water, or when heated. (Wanklyn and Carius, Ann. Ch. Pharm. cxx. 74.)

IRON, IODIDES OF. *Ferrous Iodide*, FeI or $FfeI^2$, obtained by heating or triturating iodine with a slight excess of iron filings, is a brown compound, which melts at a red heat, forms a grey laminar mass on cooling, and volatilises at a stronger heat. It dissolves readily in water, and the pale green solution, which may also be formed directly by digesting 1 pt. iron and from 2 to 4 pts. iodine in water, yields, when evaporated in contact with iron, and protected from the air, green deliquescent crystals, containing $2FeI.5H^2O$ or $FfeI^2.5H^2O$. Both crystals and solution, when exposed to the air, very quickly turn brown, from formation of oxyiodide, and separation of ferric hydrate and iodine. Ferrous iodide cannot, therefore, be easily kept unaltered, either in the solid state or in solution; it keeps best when mixed with a sufficient quantity of common sugar or milk-sugar. For preparing the compound for medical use, Mohr recommends that 1 pt. iodine be converted into ferrous iodide by trituration with iron and water, the filtered liquid mixed with 25 pts. of simple syrup, and the whole quickly evaporated down to 25 pts.; 20 pts. of this syrup contain 1 pt.

of ferrous iodide. It is best, however, to prepare the compound fresh every time it is wanted, which is not difficult, as the action is very quick.

The solution of ferrous iodide treated with alkaline carbonates, yields iodides of the alkali-metals, and may be used for the preparation of those compounds.

Ferrous iodide easily dissolves an excess of iodine: on adding 1 at. iodine to 3 at. ferrous iodide, a brown solution is formed (containing Fe^3I^4), which, when mixed with carbonate of potassium, yields iodide of potassium and black ferroso-ferric hydrate; it is doubtful whether the brown solution contains iodated ferrous iodide, or a ferroso-ferric iodide, analogous to the magnetic oxide.

Ferric iodide, Fe^2I^3 or $FfeI^3$, is not known with certainty, but appears to be formed when iron is heated in excess of iodine-vapour. The resulting compound dissolved in water, yields a brown-red solution, which reacts like that which is obtained by dissolving iodine in ferrous iodide, as above, or by dissolving ferrous hydrate in hydriodic acid. All these solutions, when exposed to the air, give off iodine and deposit ferric hydrate.

IRON, METEORIC. See p. 336.

IRON, NATIVE. See p. 335.

IRON NATROLITE. See NATROLITE.

IRON, NITRIDE OF. Iron heated to dull redness in a porcelain tube, and subjected to the action of ammonia gas, becomes white, brittle, and increases in weight by about 12 per cent. The compound thus formed is supposed by Despretz (Ann. Chim. Phys. [2] xlii. 122) to be a nitride of iron; but it has not been analysed, and is supposed by some chemists to contain hydrogen. It dissolves in weak acids, with evolution of hydrogen and nitrogen, and formation of ammoniacal salts. At a white heat it decomposed, giving off its nitrogen. Hydrogen, at a red heat, withdraws the nitrogen, forming ammonia.

Sometimes the iron, after ignition in ammonia-gas, is found to be altered in physical properties, and yet not to have increased in weight; in such a case, the combination of the nitrogen with the iron is but transient, but nevertheless appears to alter its molecular structure.

Nitride of iron is also produced when oxide of iron is ignited in ammonia gas; also in minute quantity when nitrogen gas is passed over red-hot iron. (Pelouze et Frémy. *Traité*, ii. 452.)

Respecting the controversy about the existence of nitrogen in steel, see STEEL.

IRON, NITROSULPHIDES OF. *Nitrosulfures de fer.* (Roussin, Ann. Ch. Phys. [3] lii. 285.)—Compounds produced by the simultaneous action of nitrites and alkaline sulphides on iron-salts. They contain nitric oxide, together with sulphide of iron and sulphide of hydrogen or an alkali-metal, and may therefore perhaps be regarded as analogous in composition to the nitroferricyanides (ii. 250), that is to say, as sulphides of iron in which 1 at. sulphur is replaced by 2 at. *nitrosyl*, NO. They contain in fact a disulphide of iron, Fe^2S^2 or Ffe^2S^4, in which the fourth, or sometimes the half, of the sulphur may be supposed to be replaced by an equivalent quantity of nitrosyl. The analogy of the nitrosulphides to the nitroferricyanides is shown by the fact, that when a solution of nitroferricyanide of sodium is completely decomposed by sulphydric acid, and the solution boiled and evaporated, the residue contains dinitrosulphide of iron, which may be reconverted into a nitroferricyanide by treating it with cyanide of potassium. A mixture of iron-salt and nitrite of potassium yields a nitroferricyanide when treated with cyanide of potassium, and nitrosulphide of iron when treated with sulphide of potassium. In neither of these classes of compounds can the iron be detected by ordinary reagents.

Dinitrosulphide of Iron, $Fe^6S^5H^2(NO)^4 = Ffe^2S^3(NO)^2.FfeS(NO^2)^2.H^2S$, or $Ffe^3S^4(NO)^4.H^2S$.—This compound is prepared by dropping a solution of ferric chloride or sulphate, with constant stirring, into a mixture of the solutions of nitrite of potassium and sulphide of ammonium, heating the liquid to boiling, keeping it at the boiling heat for a few minutes, and filtering to separate sulphur; the deep-coloured liquid deposits crystals of the compound on cooling.—Or 35 grms. ferrous sulphate dissolved in 0·2 litre of deaërated water is added to a solution of 21 grms. dry nitrite of potassium, and 15 grms. crystallised sulphide of sodium also in 0·2 litre of water, and the solution is boiled and filtered. When a ferrous salt is used in the preparation, no separation of sulphur takes place. The crystals are purified by recrystallisation.

Dinitrosulphide of iron forms black, needle-shaped, oblique rhombic prisms, 2 mm. long, more soluble in hot (about 2 pts.) than in cold water, easily soluble in alcohol, wood-spirit, amylic alcohol, and glacial acetic acid; they dissolve in all proportions in ether, and deliquesce even in ether-vapour. The solutions are very deep-coloured, taste styptic at first, then persistently bitter; they remain unaltered in air containing ammonia, and may be recrystallised from alkaline solutions. When heated to 115°—140°, they give off reddish vapours, together with sulphur, sulphite of ammonium, and nitrite of ammonium, and leave iron in the residue; when quickly heated, they burn away. The compound is easily decomposed by mineral acids, with evolution of reddish vapours, not by organic acids. Chlorine and iodine decompose it, with evolution of nitric oxide and separation of sulphur. It is precipitated from solution by potash and ammonia, much more slowly by soda. The crystals are decomposed by permanganate of potassium, peroxide of lead, and mercuric oxide. Many metallic salts precipitate the solution, with elimination of nitric oxide. Cyanide of potassium and cyanide of mercury convert the crystals into nitroferricyanides.

The crystals are not decomposed by sulphide of ammonium, sulphydric acid, ferro- or ferri-cyanide of potassium, or tannic acid, neither of these reagents giving any indication of the presence of iron in them. Neither are they decomposed by caustic potash or soda in the cold, but when heated therewith, they give off ammonia gas and yield ferric hydrate, together with a filtrate which deposits the following compound.

Sulphuretted Nitrosulphide of Iron and Sodium, $Fe^4Na^6N^2S^6O^2$ or $Ffe^2S^3(NO)^2.3Na^2S$.—This compound forms large black crystals having a very bitter taste, easily soluble in water and in alcohol, but insoluble in ether. The crystals decompose at 120°; their solution is decomposed, with evolution of nitric oxide, by chlorine, iodine, or mercuric oxide. It forms precipitates with metallic salts, the reaction being in some cases attended with evolution of nitric oxide. The solution yields crystalline compounds on addition of potash or ammonia, but is not altered by caustic soda; the crystals are not altered by sulphide of ammonium or ferrocyanide of potassium, but with ferricyanide of potassium they yield nitric oxide gas and prussian-blue.

Sulphuretted Nitrosulphide of Iron and Hydrogen, $Fe^4H^8N^2S^7O^2 = Ffe^2S^3(NO)^2.4H^2S$(?), separates in reddish flocks, when the preceding compound is decomposed by acids, but gives off sulphydric acid and suffers further decomposition, even during washing.

Nitrosulphide of Iron, $Fe^4S^3(NO)^2$ or $Ffe^2S^3(NO)^2$, separates, with evolution of sulphydric acid, when sulphuretted nitrosulphide of iron and sodium is decomposed by an acid at the boiling heat. It is a black substance, which when freshly prepared and dried, burns away like tinder, when set on fire. It decomposes spontaneously, leaving sulphide of iron. It is insoluble in water, alcohol, and ether, but dissolves in caustic potash, with partial decomposition and separation of ferric hydrate.

Nitrosulphide of Iron and Sodium, $Fe^4Na^2N^2S^4O^2.H^2O = Ffe^2S^3(NO)^2.Na^2S.H^2O$.—Formed by evaporating a solution of nitrosulphide of iron in sulphide of sodium at 100°, and treating the residue with alcohol and ether. Crystallises in red prisms, black by reflected light; dissolves with deep red colour in water, alcohol, and ether, but is insoluble in chloroform and in sulphide of carbon. The solution is precipitated by metallic salts, forming insoluble compounds in which the sodium is replaced by the other metal. Some of these precipitates are tolerably permanent, whereas others, the silver precipitate for example, decompose quickly, with evolution of nitric oxide.

IRON ORES. The ferruginous minerals containing sufficient quantities of iron to be available for the extraction of the metal, have already been described (pp. 337—343). For the methods of assaying them, see p. 388.

The following mineralogical terms must here be noticed.

Argillaceous or Clay Iron Ore.—This term is applied to several ores consisting of oxide or carbonate of iron mixed with clay. The argillaceous carbonate is called simply "clay iron-stone;" anhydrous and hydrated ferric oxides with a similar admixture, are called "red clay iron-stone," and "brown or yellow clay iron-stone," respectively.

Azotomous Iron Ore, or *Kibdelophane*. A variety of ilmenite or titaniferous iron ore. (See TITANATES.)

Bog Iron Ore.—A brittle or loosely aggregated variety of brown hæmatite, occurring in low marshy grounds. It proceeds from the decomposition of other species and often takes the form of leaves, nuts, or stems, found in the marshy soil.

Brown Iron Ore.—Hydrated ferric oxide (p. 338).

Columnar Iron Ore.—Red clay iron stone, having a columnar structure.

Green Iron Ore.—Hydrated ferric phosphate. (See DUFRENITE, ii. 347.)

Jaspery Iron Ore.—A variety of red clay iron ore, having a large, flat conchoïdal fracture.

Lenticular Iron Ore.—A variety of red clay iron-stone having a flat granular structure.

Magnetic Iron Ore.—Ferroso-ferric oxide (pp. 337, 397).

Micaceous Iron Ore.—Specular iron ore with a micaceous structure.

Ochreous Iron Ore.—Red hæmatite, having a soft earthy consistence.

Octahedral Iron Ore.—Syn. with magnetic iron ore.

Pitchy Iron Ore.—A variety of red hæmatite.

Red Iron Ore.—Native ferric oxide (p. 337).

Sparry or Spathic Iron Ore.—Crystallised ferrous carbonate (i. 785).

Specular Iron Ore.—Red hæmatite having a perfect metallic lustre (pp. 338, 394).

Titaniferous Iron Ore.—Ferric titanate. (See TITANATES.)

IRON, OXIDES OF. Iron forms two oxides corresponding with the chlorides, viz. the *protoxide* or *ferrous oxide*, Fe^2O or FfeO, the *sesquioxide* or *ferric oxide*, Fe^4O^3 or Ffe^2O^3, and several oxides of intermediate composition, called *ferroso-ferric oxides*, which may be regarded as compounds of the two just mentioned: the most important of these is the *magnetic oxide*, Fe^6O^4 or $Ffe^3O^4 = FfeO.Ffe^2O^3$. A *trioxide*, Fe^2O^3 or $FfeO^3$, may be supposed to exist in the ferrates (ii. 636); *e.g.* ferrate of potassium, $K^2FfeO^4 = K^2O.FfeO^3$, but it has not been isolated.

Ferrous oxide, Fe^2O or FfeO, is never found in nature in the free state, but may be supposed to exist, in combination with carbonic anhydride, as ferrous carbonate ($FfeCO^3 = Ffe^2O.CO^2$) in spathic iron ore, and in solution in chalybeate waters; also combined with ferric oxide in magnetic iron ore. It is not easily obtained in the pure state, on account of the avidity with which it absorbs oxygen. According to Debray, it is obtained by passing a mixture of equal volumes of carbonic anhydride and carbonic oxide over red-hot ferric oxide. According to Liebig, it is obtained, mixed with a little metallic iron, by igniting ferrous oxalate in a close vessel. The impure ferrous oxide thus obtained is a black pyrophoric powder, which in contact with the air quickly takes fire, and is converted into ferric oxide.

Hydrated Ferrous Oxide, or *Ferrous hydrate*, is obtained by precipitating the solution of a pure ferrous salt, perfectly free from air, with potash-ley, also free from air, in a vessel filled with de-aërated water. The hydrate is then precipitated in white flocks, which must be washed by decantation with recently boiled water, then dried and preserved in an atmosphere perfectly free from oxygen. Schmidt (Ann. Ch. Pharm. xxxvi. 101), by a very careful preparation thus conducted, obtained the hydrate as a non-magnetic, very friable mass, having a pale greenish colour, probably arising from partial oxidation. When exposed to the air, even in the dry state, it quickly absorbs oxygen, becoming strongly heated, even to ignition, and is converted into ferric oxide. In the moist state it is converted by oxidation, first into greenish ferroso-ferric, then quickly into brown ferric hydrate. It reduces iodic acid, also platinum- and mercury-salts. It dissolves, according to Bineau, in 150,000 pts. of water, forming an alkaline liquid. It dissolves easily in acids, forming ferrous salts, and absorbs carbonic anhydride quickly, even in the dry state, so that it cannot be dried in an atmosphere of that gas.

Ferrous salts.—Ferrous oxide and hydrate dissolve in acids, forming salts in which the iron is mono- or di-atomic, according as its atomic weight is 28 or 56: *e.g.*

$$\left.\begin{array}{r} Fe^2O \\ \text{or } FfeO \end{array}\right\} + 2HCl = H^2O + \left\{\begin{array}{l} \quad 2FeCl \\ \text{or } FfeCl^2. \end{array}\right.$$

$$\left.\begin{array}{r} Fe^2O \\ \text{or } FfeO \end{array}\right\} + H^2SO^4 = H^2O + \left\{\begin{array}{l} \quad Fe^2SO^4 \\ \text{or } FfeSO^4. \end{array}\right.$$

The soluble ferrous salts are likewise produced by dissolving iron in dilute acids. The insoluble salts, *e. g.* the carbonate and phosphate, are obtained by precipitation. The carbonate is of frequent occurrence as a natural mineral (p. 339).

Most ferrous salts are soluble and crystallisable, white in the anhydrous, pale greenish-blue in the hydrated state. The solutions are green or greenish-blue, have a sweetish taste, with inky after-taste, and quickly absorb oxygen from the air, yielding a yellow-brown deposit of basic ferric salt, because the quantity of acid in the solution is not sufficient to form a normal ferric salt, inasmuch as iron (Ffe) is triatomic in the ferric, and only diatomic in the ferrous salts; thus ferrous sulphate yields by oxidation a basic ferric sulphate, or oxysulphate containing only 2 at. SO^4;

$$2(FfeO.SO^3) + O = Ffe^2O^3.2SO^3,$$

or

$$2FfeSO^4 + O = Ffe^2\left\{\begin{array}{l} 2SO^4 \\ O, \end{array}\right.$$

whereas the soluble normal ferric sulphate has the composition $Ffe^2O^3.3SO^3$ or $Ffe^2(SO^4)^3$.

Those ferrous salts which contain a volatile acid, give it up on ignition, leaving a residue of ferric oxide, if the acid, such as sulphuric or nitric acid, gives up its oxygen readily; of ferroso-ferric oxide, if the acid, such as carbonic acid, retains its oxygen more forcibly; and of metallic iron, either pure or mixed with ferrous oxide, if the acid is organic.

For the reactions of ferrous salts in solution, see p. 381.

Ferric oxide. Fe^4O^3 or Ffe^2O^3. *Sesquioxide* or *peroxide of iron.* This oxide occurs in nature very abundantly and widely distributed, viz. 1. As specular iron ore in rhombohedral forms, R . oR, also R . $\frac{4}{3}$P2 . $\frac{1}{4}$R (ratio of principal to secondary axes = 1·3668 : 1).—2. As martite, in regular octahedrons.—3. As red hæmatite, in columnar, granular, botryoïdal, and stalactitic shapes, also lamellar and granular, either alone or associated with clay, forming the several varieties of red clay iron-stone

(p. 340). It is formed by heating iron or its lower oxides and hydrates in contact with the air.

Ferric oxide may be obtained in small crystals by decomposing ferric chloride with lime at a red heat (Daubré, Compt. rend. xlix. 143); in micaceous laminæ by heating the amorphous oxide with borax, and treating the resulting mass with hydrochloric acid (Hauer, Wien. Akad. Ber. xiii. 456), or by melting the amorphous oxide with chloride of calcium (Kuhlmann, Compt. rend. lii. 1283). Rhombohedral or laminar crystals of ferric oxide are likewise obtained by igniting the amorphous oxide in a slow current of hydrochloric acid gas. (Deville, Compt. rend. lii. 1264.)

When equal parts of ferrous sulphate (green vitriol) and common salt are heated to redness, and the product exhausted by washing, ferric oxide remains in red-brown shining scales. When pulverulent ferric oxide is ignited with sal-ammoniac, part of it becomes crystalline, while another portion volatilises as ferric chloride.

Ferric oxide is obtained in the amorphous state by igniting ferrous sulphate with $\frac{1}{15}$ pt. of saltpetre, and lixiviating the product; by dissolving iron in nitric acid, evaporating, and heating the resulting nitrate to redness; also by deflagrating iron filings with saltpetre. In the distillation of fuming sulphuric acid from green vitriol, a residue of impure ferric oxide is obtained, formerly known as *Caput mortuum vitrioli*. Amorphous ferric oxide is usually prepared for pharmaceutical use by igniting ferric hydrate or ferrous carbonate in contact with the air; the preparation thus obtained is called *Crocus Martis adstringens* or *Ferrum oxydatum rubrum*. Very pure ferric oxide may be prepared by heating ferrous oxalate in contact with the air; the salt then takes fire and is completely converted, without further heating, into ferric oxide. (A. Vogel.)

Ferric oxide prepared by either of the latter methods, is amorphous, and has a brown-red, red, or nearly black colour, according to the particular mode of preparation adopted. It is very hygroscopic, not magnetic, very hard, and is therefore used as a grinding and polishing material. The specific gravity of the artificially prepared oxide is 5·04 to 5·17 (H. Rose, Pogg. Ann. lxxiv. 440); that of red hæmatite and specular iron ore, from 4·5 to 5·3; of some columnar varieties as low as 4·2; that of martite from Peru, 3·80; from Puy de Dome, 4·65; from Brazil, 4·80 (Breithaupt); from Monroe, New York, 5·33 (Hunt). Hardness of hæmatite and specular iron ore = 5·5 to 6·5; of martite = 6. The cubic expansion of ferric oxide = 0·00004 for 1° C. (Kopp). Ferric oxide is not volatile, but at a full white heat it gives off oxygen, and is partially converted into ferroso-ferric oxide, which is attracted by the magnet.

Ferric oxide is reduced to the metallic state by *hydrogen gas*, at a heat even below redness, and completely at red heat by *charcoal* or *carbonic oxide*, also by *ammonia gas*. When ignited with *sulphur*, it yields sulphurous anhydride and a sulphide of iron. It easily gives up its oxygen when ignited with *combustible bodies*, but takes it up again when heated in contact with the air: hence it facilitates the combustion of organic bodies, and may be used for incinerating them (Gräger, Ann. Ch. Pharm. cxi. 124). Even at ordinary temperatures, it frequently acts as an oxidising agent in contact with organic matter, and is thereby reduced to magnetic oxide, or even to ferrous oxide, and then, by taking up carbonic acid, converted into spathic iron; the reduced oxide, if in contact with moisture, is frequently also reconverted into ferric hydrate (limonite or brown hæmatite) by atmospheric oxidation. The oxide is also sometimes further reduced by the action of *sulphydric acid*, and converted into pyrites: hence magnetite, limonite, and pyrites often occur as pseudomorphs after red hæmatite. According to Kuhlmann (Compt. rend. lii. 1169), it easily converts *sulphide of calcium* into gypsum at the expense of atmospheric oxygen; the oxysulphide of calcium of the soda-residues mixed with an equal weight of ferric oxide (the residue of the burning of pyrites), forms a very useful cement, which hardens quickly in contact with the air.

Ferric oxide dissolves in *acids*, but less easily in proportion as it has been more strongly ignited: the best solvent for it is strong boiling hydrochloric acid. The solution is facilitated by the addition of zinc or stannous chloride, the oxide then dissolving as ferrous chloride.

Ferric oxide, on account of its hardness, is much used as a grinding and polishing material. A very hard compact kind of red hæmatite, called bloodstone, forms, when well polished, the best material for producing a high lustre on coat-buttons, and on the gilding of porcelain. Ferric oxide in the pulverulent state is used for polishing gold, silver, and other metals, for polishing and sharpening cutting instruments, and for grinding and polishing glass for mirrors and lenses. According to Vogel (Dingl. pol. J. cxxxii. 275), the oxide obtained by the combustion of ferrous oxalate (p. 393) is peculiarly adapted for these purposes. That which is prepared by igniting green vitriol in crucibles is also much used, the least calcined portions, which are of a scarlet colour, forming *jeweller's rouge* for polishing gold or silver, and the more calcined portions, which are bluish or purplish, forming the *crocus* which is used for polishing brass and steel. Lord **Rosse** prepares ferric oxide for polishing the specula of his telescopes, by precipitating a pure dilute solution of ferrous sulphate with ammonia, pressing the washed precipitate in a screw-press till nearly dry, and exposing it to a heat which appears dull red in the dark. (See *Ure's Dictionary of Arts*, iii. 369.)

Ferric oxide is also used as a colouring material for glass and porcelain, especially the latter; it yields a fine purple-red, or when more strongly heated, an orange-yellow enamel colour, the tint produced depending essentially on the mode of treatment; according to **Bontemps** (Phil. Mag. [4] xxxv. 439), ferric oxide may be made to colour glass with all the tints of the spectrum, according to the degree of heat applied.

Hydrated ferric oxide, or ***Ferric hydrate***, occurs abundantly in nature, either crystallised as **göthite** or **needle iron ore** (ii. 940), or in stellate groups of needles or fibres, as **xanthosiderite**, or more frequently in stalactitic, botryoïdal or mammillary forms, having a fibrous or subfibrous structure; also massive and occasionally earthy, as **brown hæmatite** or **limonite**; also mixed with clay, as **brown** or **yellow clay iron-stone** (pp. 338, 339). It is the colouring principle of many minerals, of ochre, of the deposit of mineral waters, of yellow sandstone, Turkish umber, &c. It is formed by the precipitation of ferric salts with alkalis or alkaline carbonates; also when ferrous salts are precipitated in like manner, and the precipitate is exposed to the air; and by the rusting of iron, which takes place when the metal is exposed to moist air, and is accelerated by contact with small quantities of acids, and of various saline solutions, especially ammoniacal salts and urine.

Ferric hydrate is most easily prepared by precipitating a moderately dilute solution of ferric chloride with excess of ammonia (with a smaller quantity, a basic salt would be thrown down); it is apt, however, to retain small quantities of ammonia, to remove which it must be washed several times with water, then dried, and washed completely after being reduced to powder. This precipitate formed in the cold (the *Ferrum oxidatum fuscum* of the pharmacopœias) has the composition $Ffe^2O^3.2H^2O$, according to **Gmelin** (*Handbook*, v. 198) and **Lefort** (J. pr. Chem. liv. 305); $Ffe^2O^3.3H^2O$, according to **Wittstein** (Pharm. Centr. 1853, p. 367); or $2Ffe^2O^3.3H^2O$, according to **Péan de Saint-Gilles**, Ann. Ch. Phys. [3] xlvi. 47), the proportion of water doubtless varying according to the degree of dilution, the mode of precipitation, and the temperature to which the hydrate has been exposed in drying. The hydrate precipitated from hot solutions is $Ffe^2O^3.2H^2O$. (**Lefort**; **Schaffner**, Ann. Ch. Pharm. li. 117.)

Native ferric hydrates are also of various composition. Göthite is $Ffe^2O^3.H^2O$; limonite, $2Ffe^2O^3.3H^2O$; xanthosiderite, $Ffe^2O^3.2H^2O$; and a variety of bog iron ore (called *Quellerz*) from Nischnei-Nowgorod in Russia, consists, according to **Hermann** (J. pr. Chem. xxvii. 53), mainly of $Ffe^2O^3.3H^2O$.

Ferric hydrate has a light yellow to dark brown colour, and is sometimes a loose earthy powder, sometimes a heavy friable mass, according to the mode of preparation. When recently precipitated, it is easily soluble in acids, but its power of uniting with acids is diminished by drying, and frequently even by prolonged immersion in liquids.

A remarkable insoluble modification of ferric hydrate is produced by boiling the ordinary yellow hydrate, $2Ffe^2O^3.3H^2O$ (precipitated from the chloride by ammonia), in water for seven or eight hours. The colour then changes from ochre-yellow to brick-red, and the hydrate thus altered is scarcely acted upon by strong boiling nitric acid, and but very slowly by hydrochloric acid. In acetic acid, or dilute nitric or hydrochloric acid, it dissolves, forming a red liquid, which is clear by transmitted, but turbid by reflected light; is precipitated by the smallest quantity of an alkali-salt or a sulphate; and on addition of strong nitric or hydrochloric acid, yields a red granular precipitate, which redissolves on diluting the liquid with water. The modified hydrate does not form prussian blue with ferrocyanide of potassium and acetic acid. It appears to consist of $Ffe^2O^3.H^2O$. This insoluble hydrate is likewise precipitated when a solution of the ordinary hydrate in acetic acid is rapidly boiled. The same solution, if kept for some time at 100° C. in a close vessel, becomes light in colour, no longer forms prussian blue with ferrocyanide of potassium, or exhibits any deepening of colour on addition of a sulphocyanate; strong hydrochloric or nitric acid, or a trace of an alkali-salt, or sulphuric acid, throws down all the ferric oxide in the form of the insoluble hydrate. (**Péan de Saint-Gilles**, Ann. Ch. Phys. [3] xlvi. 47.)

Ferric hydrate gives off part of its water between 80° and 100°, and the whole at a red heat; it is also completely dehydrated by heating it to 160°—200°, with a saturated solution of chloride of calcium or chloride of sodium. (**Senarmont**.)

Ferric hydrate easily gives up part of its oxygen to oxidable bodies, and is easily reduced by sulphurous acid, stannous chloride, &c. In contact with putrefying organic bodies, out of contact with the air, it forms ferroso-ferric compounds, or ferrous carbonate; but if the air has access to it, it quickly recovers the oxygen which it has given up to the putrefying substance, and can then again exert an oxidising action, thus acting as a carrier of oxygen from the air to the organic body: hence it accelerates the oxidation of woody fibre in the soil. (Kuhlmann, J. pr. Chem. lxxxi. 110.)

Ferric hydrate is rarely used alone in medicine; but in the recently precipitated state, it acts as an antidote to arsenic, as, when given in sufficient quantity, it forms a highly basic ferric arsenite, very difficultly decomposible by water.

Ferric hydrate unites with colouring matters, and easily fixes itself on many organic bodies, especially on tissues: hence its use as a mordant, and the formation of iron-mould on linen, cotton. Such spots may be removed by oxalic acid, or acid oxalate of potassium, the action being greatly accelerated by contact with metallic tin.

Ferric salts.—In these salts, the iron is sesqui- or tri-atomic, according as its atomic weight is 28 or 56, *e.g.* the chloride, Fe^2Cl^3 or $FfeCl^3$; the nitrate, $Fe^2(NO^3)^3$ or $Ffe(NO^3)^3$; the sulphate, $Fe^4(SO^4)^3$ or $Ffe^2(SO^4)^3$. (The oxygen-salts may, of course, be regarded as compounds of ferric oxide with anhydrous acids. *e.g.* the nitrate, $Ffe^2O^3.3N^2O^5$, the sulphate, $Ffe^2O^3.3SO^3$.) Accordingly, it requires three molecules of a monobasic acid, such as nitric acid, to form a normal salt with one molecule of ferric oxide.

The normal ferric salts are for the most part soluble in water, and difficult to crystallise; some of them are deliquescent. They are mostly analogous in composition to the salts of aluminium, and frequently isomorphous with them; this correspondence of form and composition is most conspicuous in the alums; thus ferrico-potassic-sulphate, $FfeK(SO^4)^2.12H^2O$, is isomorphous with common alum, $AllK(SO^4)^2.12H^2O$.

Soluble ferric salts are obtained by dissolving ferric oxide or its hydrates in aqueous acids, or by oxidising ferrous salts with nitric acid, adding the quantity of acid required to form a normal ferric salt; *e.g.*:

$$2FfeSO^4 + O + H^2SO^4 = Ffe^2(SO^4)^3 + H^2O.$$

The insoluble salts are obtained by double decomposition.

Ferric salts are white in the anhydrous, yellow or yellowish-red in the hydrated state. The solutions have also, for the most part, a yellowish-red colour, especially when heated; the solutions of the nitrate and fluoride, however, are colourless; that of the chloride is brown-red, and those of the acetate, meconate, and sulphocyanate are blood-red.

The presence of free hydrochloric acid in a solution of ferric chloride changes the colour of the solution to orange yellow; this coloration, like that of other acid solutions of ferric salts (*e. g.* ferric sulphocyanates) is completely destroyed by addition of a sufficient quantity of phosphate of sodium; on the other hand, the colouring power of ferric chloride, in presence of an excess of strong hydrochloric acid, is very great, the bright yellow colour of commercial hydrochloric acid, for instance, being caused by a quantity of ferric chloride too small to impart a perceptible colour to the liquid when somewhat diluted with water.

Ferric oxide has a great tendency to form basic salts, which may be regarded as compounds of the normal salts with excess of ferric oxide: thus, besides the triacid or normal sulphate,

$Ffe^2O^3.3SO^4 = \overset{\prime\prime\prime}{Ffe}{}^2(SO^4)^3 = \left.\begin{matrix}(\overset{\prime\prime}{S}O^2)^3\\ \overset{\prime\prime\prime}{Ffe}{}^2\end{matrix}\right\}O^6$, there are several basic sulphates, viz.:

Sexbasic, $6Ffe^2O^3.SO^3 = \left.\begin{matrix}\overset{\prime\prime}{S}O^2\\ \overset{\prime\prime\prime}{Ffe}{}^{12}\end{matrix}\right\}O^{19}$ or $17Ffe^2O^3.Ffe^2(SO^4)^3$

Quadribasic, $4Ffe^2O^3.SO^3 = \left.\begin{matrix}\overset{\prime\prime}{S}O^2\\ \overset{\prime\prime\prime}{Ffe}{}^{8}\end{matrix}\right\}O^{13}$ or $11Ffe^2O^3.Ffe^2(SO^4)^3$

Tribasic, $3Ffe^2O^3.SO^3 = \left.\begin{matrix}\overset{\prime\prime}{S}O^2\\ \overset{\prime\prime\prime}{Ffe}{}^{6}\end{matrix}\right\}O^{10}$ or $8Ffe^2O^3.Ffe^2(SO^4)^3$

Dibasic, $2Ffe^2O^3.SO^3 = \left.\begin{matrix}\overset{\prime\prime}{S}O^2\\ \overset{\prime\prime\prime}{Ffe}{}^{4}\end{matrix}\right\}O^{7}$ or $5Ffe^2O^3.Ffe^2(SO^4)^3$

Monobasic, $Ffe^2O^3.SO^3 = \left.\begin{matrix}\overset{\prime\prime}{S}O^2\\ \overset{\prime\prime\prime}{Ffe}{}^{2}\end{matrix}\right\}O^{4}$ or $2Ffe^2O^3.Ffe^2(SO^4)^3$

Sesquiacid, $2Ffe^2O^3.3SO^3 = \left.\begin{matrix}(\overset{\prime\prime}{S}O^2)^3\\ \overset{\prime\prime\prime}{Ffe}{}^{4}\end{matrix}\right\}O^{9}$ or $2Ffe^2O^3.2[Ffe^2(SO^4)^3]$

Diacid, $Ffe^2O^3.2SO^3 = \left.\begin{matrix}(\overset{\prime\prime}{S}O^2)^2\\ \overset{\prime\prime\prime}{Ffe}{}^{2}\end{matrix}\right\}O^{5}$ or $Ffe^2O^3.2[Ffe^2(SO^4)^3]$

Most of these basic salts are insoluble in water, and are precipitated on heating a moderately dilute and nearly neutral solution of the corresponding normal salt (*e.g.* ferric acetate), or on adding to the solution of a normal ferric salt, a quantity of alkali not sufficient to precipitate the whole.

Ferric salts containing volatile acids are decomposed by ignition, leaving a residue of ferric oxide, ferrous oxide, or metallic iron, according to the nature of the acid present. For their reactions before the blowpipe and in solution, see page 380.

Ferroso-ferric Oxides and Hydrates.—The term ferroso-ferric is applied to oxides of iron which are intermediate in composition between ferrous and ferric oxide, and may be regarded as compounds of the two. The principal of these intermediate oxides are the scale-oxide and the magnetic oxide.

α. *Scale oxide*, $Fe^{16}O^{9}$ or $Ffe^{8}O^{9} = 6FfeO.Ffe^{2}O^{3}$.—When iron is heated to redness in the air, two layers of scale oxide are formed, which may easily be separated. The inner layer, $6FfeO.Ffe^{2}O^{3}$, is blackish-grey, porous, brittle, and attracted by the magnet. The outer layer contains a larger quantity of ferric oxide, but in variable proportion; it is of a reddish iron-black colour, dense, brittle, yields a black powder, and is more strongly attracted by the magnet than the inner layer. The amount of ferric oxide in the outer layer is between 32 and 37 per cent., and on the very surface it is as much as 52·8 per cent. (Mosander, Pogg. Ann. vi. 35; also Schw. xlvii. 81). The specific gravity of the scale-oxide is 5·48 (P. Boullay). Berthier (Ann. Ch. Phys. [2] xxvii. 19; also Schw. xliii. 319) regards the scale-oxide as $4FfeO.Ffe^{2}O^{3}$; Mosander attributes the greater amount of ferric oxide found by Berthier to the fact of Berthier having analysed the inner and outer layers together.

β. *Magnetic oxide*, $Fe^{3}O^{2}$ or $Ffe^{3}O^{4} = \left.\begin{matrix}\overset{\prime\prime}{Ffe}\\ \overset{\prime\prime\prime}{Ffe}{}^{2}\end{matrix}\right\}O^{4} = FfeO.Ffe^{2}O^{3}$.—This oxide occurs abundantly as a natural mineral, and is one of the richest and most valuable ores of iron, containing, when pure, nearly 72 per cent. of the metal (p. 337). It occurs in monometric crystals, the dominant form being usually the octahedron, sometimes the rhombic dodecahedron, these forms being modified as in figures 194, 195, 196, 199, 200, &c. (CRYSTALLOGRAPHY, ii. 129, 130); twins also occur, like figure 319 (ii. 160). It is isomorphous with spinel $\left.\begin{matrix}\overset{\prime\prime}{Mmg}\\ \overset{\prime\prime\prime}{All}{}^{2}\end{matrix}\right\}O^{4}$, gahnite, $\left.\begin{matrix}\overset{\prime\prime}{Zzn}\\ \overset{\prime\prime\prime}{All}{}^{2}\end{matrix}\right\}O^{4}$, zeilanite, $\left.\begin{matrix}\overset{\prime\prime}{Ffe}\\ \overset{\prime\prime\prime}{All}{}^{2}\end{matrix}\right\}O^{4}$, franklinite, $\left.\begin{matrix}\overset{\prime\prime}{Zzn}\\ \overset{\prime\prime\prime}{Ffe}{}^{2}\end{matrix}\right\}O^{4}$, chrome-iron ore, $\left.\begin{matrix}\overset{\prime\prime}{Ffe}\\ \overset{\prime\prime\prime}{Ccr}{}^{2}\end{matrix}\right\}O^{4}$, and other minerals in which the diatomic radicles, Mmg, Zzn, Ffe, and likewise the triatomic radicles, All, Ffe, Ccr, replace one another in various proportions, or into which other diatomic metals enter in various proportions, *e.g.* calcium, Cca, with magnesium in pleonast and chlorospinel. Cleavage octahedral, more or less distinct. The dodecahedral faces are commonly striated, parallel to the longer diagonal. Much more frequently, however, it occurs massive, with granular structure (p. 336).

Ferroso-ferric oxide, $Ffe^{3}O^{4}$, is produced when iron is heated to redness in aqueous vapour (Regnault, Gay-Lussac); when ferrous chloride is heated to low redness with excess of carbonate of sodium (Liebig and Wöhler, Pogg. Ann. xxi. 582); also according to Mitscherlich (Pogg. Ann. xv. 622), when iron is burned in oxygen-gas or before the blowpipe. It is obtained crystallised in octahedrons, by igniting ferroso-ammonic chloride in contact with the air (Hauer, Wien. Akad. Ber. xiii. 456); also, together with ferrous chloride, by heating ferrous oxide in a slow stream of hydrochloric acid gas (Deville, Compt. rend. liii. 199); by fusing ferric phosphate with 3 or 4 times its weight of sulphate of sodium (Debray, *ibid.* lii. 985); and by heating ferrous sulphate with chloride of calcium in covered crucibles (Kuhlmann, *ibid.* lii. 1283). Deville and Caron (*ibid.* xliv. 764), by heating ferric fluoride with boric anhydride out of contact with the air, obtained the magnetic oxide in long needles, made up of aggregates of regular octahedrons. Ebelmen obtained crystalline magnetic oxide by the action of heat on ferrous silicate. Artificially prepared ferroso-ferric oxide is, however, most frequently a black mass, which yields an iron-black powder, and is attracted by the magnet.

Many metallurgic products also contain ferroso-ferric oxide, either free or combined with silica—refinery-slags for example, according to Plattner (Ann. Ch. Pharm. xx. 233). The iron plates which are laid beneath the hearths of iron-smelting furnaces, and are exposed to a red heat, are sometimes, in the course of 6 or 10 years, completely converted, by the moisture of the soil, into magnetic oxide, partly crystalline, partly compact, and attracted by the magnet (but not itself magnetic). The same compound is formed on the under side of the refining hearths, where the iron comes in contact with aqueous vapour. (Koch, *Ueber krystall. Hüttenproducte*, p. 17.)

γ. Crystallised ferrous carbonate, ignited in close vessels, yields ferroso-ferric oxide, consisting, according to Krämer, of $FfeO.Ffe^2O^3$; according to Döbereiner, of $3FfeO.Ffe^2O^3$; according to Glasson, of $4FfeO.Ffe^2O^3$, the composition of the product being doubtless influenced by the rapidity of the heating.

δ. The old pharmaceutical preparation called *Æthiops martialis*, is a ferroso-ferric oxide, or mixture of ferrous and ferric oxides in various proportions, obtained by oxidising iron in a current of aqueous vapour, or by partially reducing ferric oxide by ignition with iron filings, or with a quantity of oil just sufficient to make it into a moist powder; the preparation obtained by this last method always contains carbon.

Ferroso-ferric oxide is easily reduced to the metallic state by ignition with hydrogen, charcoal, carbonic oxide, or ammonia-gas. When ignited in the air, it is converted into ferric oxide.

Ferroso-ferric Hydrates.—These are compounds of various composition, obtained by the partial oxidation of ferrous, or reduction of ferric hydrate, by precipitating mixtures of ferrous and ferric salts with alkalis, and by the oxidation of iron in contact with air and water.

α. *Dingy-green Hydrate.*—By exposing white ferrous hydrate to the air for a short time—or by precipitating a mixture of a ferrous salt and a small quantity of ferric salt, with potash or ammonia—a dingy-green hydrate of ferroso-ferric oxide is obtained, which, on further exposure to the air, is quickly converted into rusty-brown ferric hydrate.

β. *Black Hydrate.*—1. This hydrate, which has nearly the composition $FfeO.Ffe^2O^3 + xH^2O$, is precipitated from a solution of magnetic oxide in hydrochloric acid, or from a mixture of equivalent proportions of ferrous and ferric salts, on the addition of potash or ammonia. The yellow solution of magnetic oxide in hydrochloric acid yields, with ammonia, a brownish-black precipitate, which is magnetic even while in the liquid, so that it collects round a magnet dipped into that liquid. It may be washed on the filter without becoming more highly oxidised (Liebig and Wöhler, Pogg. Ann. xxi. 583).—2. The same precipitate is obtained by mixing ferrico-ammonic sulphate with ferrous sulphate, in such proportion that the ferric oxide present in the mixture may contain three times as much oxygen as the ferrous oxide, and precipitating with ammonia (Abich, Pogg. Ann. xxiii. 354).—3. Two equal portions of ferrous sulphate are taken; the first is dissolved in water acidulated with sulphuric acid, and oxidated at a boiling heat by the addition of nitric acid in small portions at a time. The other portion is dissolved in water freed from air by boiling. The two solutions are then mixed; the mixture, while still hot, precipitated by ammonia added at once in excess; and the liquid, together with the brown-black precipitate, heated for some minutes to the boiling point. The precipitated ferroso-ferric oxide is then collected on a filter and washed—during which process it undergoes further oxidation—and then dried at a gentle heat (Wöhler, Ann. Ch. Pharm. xxii. 56). This process should yield $2FfeO.Ffe^2O^3$; but even if a greater quantity of ferric oxide is not produced by the nitric acid still remaining, or by contact with the air, the proportion of that oxide is sure to be increased by decomposition of water.—4. Böttger (*Beiträge*, ii. 12) precipitates ferrous sulphate free from ferric oxide by the addition of carbonate of sodium; washes the precipitate several times by decantation; and then boils it with tolerably concentrated caustic potash. This process yields a velvet-black powder, much less liable to absorb an additional quantity of oxygen than that which has been precipitated by ammonia.—5. Noel (J. Pharm. [3] i. 62) precipitates ferrous sulphate with carbonate of sodium, washes the ferrous carbonate by decantation, leaves it to drain upon linen, and then heats it in a cast-iron vessel, with constant stirring, till it is dry. It is thereby converted into a velvet-black powder. Soubeiran obtained by this process a precipitate which was not perfectly black, and when treated with hydrochloric acid, evolved carbonic anhydride.—6. Preuss introduces 4 pts. of pulverised iron and 5 pts. of ferric oxide into a flask, together with a two or threefold quantity of water, and boils the liquid gently for some time. The mixture gives off fetid hydrogen gas, and turns dark brown at first, but afterwards black. When the evolution of gas ceases, and the resulting black powder settles down readily, it is separated by levigation from the excess of iron; thrown on a filter of grey porous paper; and the filter, after the water has drained off, is wrapped up in a large quantity of paper, and quickly dried in hot air. The black, very loose powder dissolves in acids without evolution of gas, and the solution yields a black precipitate on the addition of an alkali. The precipitate must not be dried by heat, because in that case it would turn brown from higher oxidation. (Wöhler, Ann. Pharm. xxviii. 92.)

The black hydrate of ferroso-ferric oxide exhibits, after drying, the appearance of brown black, brittle, strongly magnetic lumps, having a conchoïdal fracture, and yielding a dark-brown powder. It contains about 7 per cent. of water, which it gives off when heated in a retort, leaving black anhydrous ferroso-ferric oxide. When heated in the air, it is converted into ferric oxide. From its yellow solution in hydrochloric acid, it is precipitated unchanged by ammonia (Wöhler).

Ferroso-ferric hydrate was formerly much employed in medicine, but has now almost fallen into disuse. In preparing iodide of potassium from iodide of iron, it is advisable to take the iron and iodine in such proportion (Fe^3I^4) that, on precipitating with carbonate of potassium, this black ferroso-ferric hydrate shall be formed, because it is much less bulky than ferric hydrate, and therefore easier to wash.

The ferroso-ferric oxides and hydrates dissolve in acids, forming brownish or yellow solutions, according as the one or other of the oxides predominates. These solutions, commonly said to contain ferroso-ferric salts, are mere mixtures of ferrous and ferric salts, and give reactions intermediate between the two. They give black precipitates with alkalis; blue, both with ferro- and with ferri-cyanide of potassium, also with cyanide of potassium (ii. 219, 227), a reaction not produced either by ferrous or by ferric salts when pure.

Trioxide of Iron, or *Ferric anhydride*, Fe^2O^3 or $FfeO^3$, is not known in the free state, but may be supposed to exist in the ferrates (salts obtained by fusing iron or its oxides with nitre, (ii. 636) *e.g. Ferrate of potassium*, $FeKO^2. = K^2O.Fe^2O^3$.

IRON, OXYBROMIDE OF. Ferric oxybromide is obtained by evaporating the aqueous solution of ferric bromide, or by treating it with a quantity of potash not sufficient for complete precipitation, or by exposing a solution of ferrous bromide to the air. (Löwig.)

IRON, OXYCHLORIDE OF. See page 378.

IRON, OXYFLUORIDE OF. A ferric oxyfluoride is precipitated by ammonia from the solution of ferric fluoride. (Berzelius.)

IRON, OXYGEN-SALTS OF. The general properties of these salts have been already described (pp. 380, 393, 396). For the special descriptions, see the several Acids.

IRON, OXYSULPHIDE OF. See page 401.

IRON, PHOSPHIDES OF. Phosphorus unites readily with iron, forming a grey, fusible, very hard compound, which takes a high polish. This compound, which has the composition Fe^4P, may be prepared by heating a mixture of phosphate of iron and charcoal in a crucible lined with charcoal and placed in a forge fire.

A very small quantity of phosphorus produces a great alteration in the properties of iron, rendering it brittle in the cold (pp. 329, 334).

IRON, PULVERISED. *Ferrum pulveratum; Limatura ferri s. Martis alcoholisata.*—Finely pulverised iron for medical use may be prepared by mechanical trituration of filings of bar iron, and subsequent boiling and straining. Iron-powder is prepared in large quantities by this method in the Tyrol. The iron is, however, obtained in a much finer state of division, by reducing an oxide of iron with hydrogen. Wöhler (Ann. Ch. Pharm. cix. 125; cv. 192) mixes 1 pt. of ferrous sulphate perfectly free from copper, with three times its weight of chloride of sodium; heats the mixture till it becomes red-hot and fuses; washes the residue completely; heats the ferric oxide thus produced to dull redness in a glass tube or gun-barrel; and passes over it a stream of dry hydrogen, perfectly free from carbon, sulphur, phosphorus, and arsenic, as these substances, if present, would unite with the iron. It is difficult, however, when ferrous sulphate is used, to obtain iron quite free from sulphur; hence, Luca (Compt. rend. li. 333) precipitates ferrous chloride with ammonia, and reduces the washed oxide with perfectly washed hydrogen-gas, avoiding the use of vulcanised caoutchouc-tubes (because the gas might take up sulphur from them). It is doubtful, however, whether the presence of minute quantities of sulphur and carbon in the pulverised iron, would be at all injurious in its application. To preserve the iron from rust, it is kept in sealed vessels filled with hydrogen.

Reduced iron is an impalpable, slate-grey powder, which may be set on fire by a glowing body, and then burns away very quickly (mechanically pulverised iron cannot be set on fire in this way); it should be heated strongly enough in the hydrogen-atmosphere to prevent it from becoming actually pyrophoric. It is much more active than mechanically pulverised iron, on account of its finer state of division.

IRON, SELENIDES OF. Selenium in the state of vapour, passed over iron-filings, combines with the metal, producing considerable evolution of light and heat. The product is a yellowish-grey substance, with metallic lustre, hard and brittle. It melts before the blowpipe, giving off oxide of selenium, and forming a black brittle globule, apparently consisting of ferrous selenite. (Berzelius.)

G. Little (Ann. Ch. Pharm. cxii. 211), by passing selenium-vapour over red-hot iron wire, and melting the brittle product under borax, obtained a metallic-looking greyish-yellow, easily pulverisable compound, having a specific gravity of 6·38, and the composition of ferric selenide, Ffe^2Se^3.

IRON, SULPHIDES OF. Iron and sulphur unite directly with one another, under various circumstances, and in several different proportions. Besides two sub-sulphides containing less than 1 at. sulphur to 1 at. iron (Ffe), there is a *protosulphide* or *ferrous sulphide*, FfeS; a *sesquisulphide* or *ferric sulphide*, Ffe^2S^3; a *disulphide*, $FfeS^2$; and a compound called the *magnetic* sulphide, intermediate in composition between the proto- and sesqui-sulphides. Metallic iron heated with excess of sulphur, yields one or other of the four last mentioned compounds, according to the heat applied, the degree of sulphuration being less as the temperature is higher. (Rammelsberg, Pogg. Ann. cxxi. 337.)

An **octoferric sulphide**, $Fe^{16}S$ or Ffe^8S, is formed by passing hydrogen-gas over red-hot dibasic ferric sulphate (p. 396). It is a blackish-grey magnetic powder, which, when treated with dilute acids, yields a mixture of 7 vols. hydrogen-gas and 1 vol. sulphydric acid.

A **hemisulphide**, Fe^4S or Ffe^2S, is produced by heating anhydrous ferrous sulphate in hydrogen gas, half of the sulphur being then given off as sulphurous anhydride. It is a dark grey, coherent, magnetic powder, which dissolves easily in dilute acids, giving off equal volumes of hydrogen and sulphydric acid. When ignited in sulphydric acid gas, it takes up sulphur and is converted into the protosulphide. It occurs, combined with other metallic sulphides, in many furnace-products obtained in the smelting of lead and copper ores.

Protosulphide, or **Ferrous sulphide,** Fe^2S or FfeS. This compound occurs in many specimens of meteoric iron, sometimes imbedded in small yellow-brown masses, sometimes as a grey powder possessing metallic lustre. (Berzelius; Rammelsberg, Pogg. Ann. cxxi. 363.)

It has not been found in the free state as a terrestrial mineral, but exists in combination with sulphide of nickel, and mixed with copper-pyrites, in a massive, bronze-coloured mineral, with octahedral cleavage and specific gravity = 4·60, from Lillehammer, in Norway. This mineral, after deducting 5·14 per cent. of copper pyrites, contains 36·7 per cent. sulphur, 41·1 iron, and 22·2 nickel, agreeing approximately with the formula $2Fe^2S.Ni^2S$. (Rammelsberg, *loc. cit.*)

Ferrous sulphide is produced: 1. By the direct combination of sulphur and iron, either at a red heat, or at lower temperatures in presence of water.—*α*. Heated iron wire introduced into sulphur-vapour burns brightly, and forms ferrous sulphide.—*β*. When iron filings are gradually heated in a covered crucible with about two-thirds their weight of sulphur, the mass, when heated to about the temperature of low-redness, begins to glow, and combination rapidly takes place, with vivid combustion throughout the entire mass.—*γ*. Sulphur pressed against a red-hot iron bar, perforates it, and forms ferrous sulphide, which runs off in drops, and may be quenched in water. *δ*. Ferrous sulphide may also be obtained in the wet way by moistening a mixture of 28 pts. iron filings and 16 pts. sulphur, and applying a gentle heat; combination then takes place, attended with considerable rise of temperature. When a considerable quantity of mixture of 2 pts. sulphur and 3 pts. iron-filings is made into a paste with water, and covered with earth, the mass after a while becomes red-hot, and gives off a large quantity of steam, which throws up the earth with violence, producing the effect of an artificial volcano.

2. By igniting ferric oxide or scale-oxide of iron with sulphur.—3. By heating iron pyrites, ferric sulphide, or magnetic pyrites, either alone to a bright red heat, or with iron filings, or in an atmosphere of hydrogen.—4. By reducing ferrous sulphate at a bright red heat in a crucible lined with charcoal. Ferrous sulphate is also reduced to sulphide in the wet way by contact with decomposing organic matter.—5. By precipitating ferrous salts with alkaline sulphides.

Ferrous sulphide prepared in the dry way is a dense yellow mass with metallic lustre, or sometimes a black porous mass. It is sometimes magnetic, but according to Berzelius, only when it contains a portion of one of the higher sulphides. It does not alter sensibly by exposure to the air at ordinary temperatures, and is not decomposed by ignition, even to whiteness, in close vessels; but when gently heated in the air, it is partly converted into ferrous sulphate; while at a stronger heat, sulphurous anhydride is evolved, and ferric oxide remains behind. With *nitric acid* it evolves nitrous gas, ferric oxide and sulphuric acid being formed, and sulphur separated. It dissolves in dilute *sulphuric* or *hydrochloric acid*, with evolution of pure sulphydric acid gas. If, however, it is mixed with metallic iron, which is generally the case with the protosulphide obtained by igniting iron filings with sulphur, it gives off a mixture of sulphydric acid and free hydrogen. *Aqueous vapour* passed over red-hot proto-sulphide of iron converts it, with evolution of much hydrogen and sulphydric acid gas, into a black and partly magnetic mass. The water forms with the sulphide of iron, sulphydric acid and ferrous oxide, which, by further decomposition of water, yields hydrogen gas and ferroso-ferric oxide; but a portion of the sulphur remains, even after three hours' ignition (Regnault, Ann. Ch. Phys. [2] lxii. 379). *Chlorine gas* does not decompose cold sulphide of iron; but that compound, when heated in the gas, yields chloride of sulphur and sublimed ferric chloride (H. Rose, Pogg. Ann. xlii. 540). Protosulphide of iron, heated to low redness with once or twice its weight of *carbonate of sodium* or *potassium*, fuses into a black, crystalline, highly magnetic mass, from which water extracts sulphide of sodium or potassium, with a trace of sulphuric acid. *Baryta* and *lime* behave in the same manner, only that the viscidity of the slag prevents the iron from fusing into a mass (Berthier, Ann. Ch. Phys. [2] xxxi. 170). When protosulphide of iron is fused with 30 times its weight of *protoxide of lead*, the whole of the sulphur is given off in the form of sulphurous anhydride, metallic lead is separated, and a fused mixture of protoxide of iron and protoxide of lead is produced.

Ferrous sulphide prepared in the wet way is a black amorphous substance, perhaps containing water; in the finely divided state, it has a dark green colour. In the moist state, it oxidises quickly on exposure to the air, being converted, first into ferrous sulphate, then quickly into yellow-brown basic ferric sulphate. It exhibits the same reactions as the protosulphide prepared in the dry way, but is much more easily decomposed, and dissolves much more quickly in acids, with violent evolution of sulphydric acid gas.

The black mud at the bottom of drains, cess-pools, ponds and morasses, owes its colour to sulphide of iron, probably formed by the putrefaction of organic matters in contact with ferric oxide contained in the soil.

Sesquisulphide or **Ferric Sulphide.** Fe^4S^3 or Ffe^2S^3.—This compound is probably a constituent of copper pyrites, $Ccu^2S.Ffe^2S^3$ (ii. 77), and of magnetic pyrites (see below). It is produced by heating iron to moderate redness, or ferric oxide to low redness with excess of sulphur: in the latter case, however, the product is mixed with ferric oxide, unless the process is several times repeated (Rammelsberg, Pogg. Ann. cxxi. 339). According to Berzelius, it may also be obtained by the action of sulphydric acid on ferric oxide at 100°, or on ferric hydrate at ordinary temperatures, or by dropping a neutral solution of ferric sulphate into excess of sulphydrate of ammonium. According to Rammelsberg, however, the product obtained by heating ferric oxide in sulphydric acid gas to a temperature short of redness, is an oxysulphide containing 1 at. ferric oxide to 3 at. ferric sulphide; after stronger heating, the product contains less ferric oxide, but in place of it a certain quantity of ferrous sulphide; and if the heat be raised to bright redness, there remains at last a sulphide of iron free from oxygen and having the composition of magnetic pyrites.

Ferric sulphide dried out of contact with air, is a yellow-grey, non-magnetic powder. When heated to redness in close vessels, it gives off sulphur and leaves magnetic pyrites. In the moist state it oxidises very quickly in contact with the air, especially when prepared by precipitation of ferric salts. Acids decompose it, with formation of ferrous salt, evolution of sulphydric acid, and precipitation of sulphur.

Ferroso-ferric or **Magnetic Sulphide.**—This sulphide occurs native as magnetic pyrites, and is formed by heating iron with a slight excess of sulphur till the mass fuses; also by heating the disulphide to redness in a covered crucible. As thus prepared, it has a brownish-yellow to speiss-yellow colour; is attracted by the magnet, and sometimes itself magnetic. It does not lose weight when simply ignited in close vessels, but when heated in *hydrogen gas*, it yields sulphydric acid and the protosulphide. Dilute *acids* dissolve it, with separation of sulphur and evolution of sulphydric acid. Boiling *potash-ley* is said to remove a portion of the sulphur, leaving ferrous sulphide.

Magnetic pyrites or Pyrrhotin occurs in crystals belonging to the hexagonal system and generally tabular, exhibiting the combinations $oP . P$, $oP . \infty P$, $oP . \infty P . P$, like figures 239, 240 (ii. 139) and others. Ratio of principal to secondary axes = 1 : 1·741. Angle $P : P$ in the terminal edges of the pyramids = 126° 49′; in the lateral edges = 127° 6′. Cleavage tolerably distinct parallel to oP, indistinct parallel to ∞P. More commonly massive and amorphous, with granular structure. Hardness = 3·5 to 4·5. Specific gravity, 4·51 to 4·64 (Rammelsberg). Lustre metallic. Colour between bronze-yellow and copper-red. Streak dark greyish-black. Fracture small subconchoïdal. Brittle. Slightly attracted by the magnet. Tarnishes quickly. Before the blowpipe it gives off sulphurous anhydride, and on charcoal in the outer flame, is converted into ferric oxide; in the inner flame it melts and continues to glow after the blowpipe is removed. The mass, after cooling, is magnetic and has a metallic crystalline structure, with a yellowish colour on the fractured surface.

The following are analyses of magnetic pyrites calculated to 100 parts, after deducting quartz, &c. (Rammelsberg, *loc. cit.*)

	H. Rose.	Schaffgotsch.	Rammelsberg.	Plattner.		Stromeyer.
	a	*b*	*c*	*d*	*e*	*f*
Fe	61·56	61·17	60·66	60·20	60·29	59·29
S	38·44	38·83	39·34	39·80	39·71	40·71

	Rammelsberg.					
	g	*h*	*i*	*j*	*k*	*l*
Fe	59·21	60·00	60·83	61·03	61·30	60·10
S	40·79	40·00	39·17	38·97	38·70	39·90

a. From Bodenmais in Bavaria; *b*, from the same; *c*, from the same; *d*, from Conghonas da Campo, Brasil; *e*, from Fahlun in Sweden; *f*, from Treseburg in the Harz; *g*, *h*, from Harzburg in the Harz; *i*, from Trumbull in Connecticut; *j*, from Xalastoc in Mexico; *k*, *l*, from localities unknown.

These results may be included under the general formula, $Fe^{2n}S^{n+1}$ or $Ffe^{2}S^{n+1}$, in which *n* may have either of the values 5, 6, 7, 8, 9, 10; but the purest specimens agree most nearly with the formula, $Ffe^{7}S^{8} = 5FfeS.Ffe^{2}S^{3}$, given by Berzelius, or with $Ffe^{8}S^{9} = 6FfeS.Ffe^{2}S^{3}$.

Nickeliferous magnetic pyrites occurs crystallised or massive and of specific gravity 4·543 to 4·674, in several localities. The following are analyses:

	Berzelius.	Scheerer.	Rammelsberg.			
	a	*b*	*c*	*d*	*e*	*f*
Fe	58·73	56·74	55·82	55·96	56·57	56·42
Ni	3·17	2·82	5·59	3·86	3·16	3·33
S	38·10	40·44	38·59	40·18	40·27	40·25
	100·00	10·000	100·00	100·00	100·00	100·00

a. Massive from Klefva in Småland, Sweden; *b*. Massive from Modum in Norway; *c*. Laminar, intergrown with quartz and mica, from the Gap mine, Pennsylvania; *d*. Massive, intergrown with white iron pyrites, also containing a small quantity of copper pyrites, from Horbach in Baden; *e*. Laminar, from Hilsen in Norway.

These analyses may be represented by the formula, $M^{5}S^{6} = 3MS.M^{2}S^{3}$, and $M^{6}S^{7} = 4MS.M^{2}S^{3}$, where M stands for Ffe (56) and Nni (58·9), each metal being present in both degrees of sulphuration. (Rammelsberg.)

Disulphide of Iron. $Fe^{2}S^{2}$ or $FfeS^{2}$.—This compound occurs abundantly in nature in two distinct forms, viz. as *Yellow Iron pyrites*, *Cubic pyrites* or *Mundic*, which crystallises in monometric forms, and *White Iron pyrites*, *Marcasite*, *Radiated pyrites*, *Spear pyrites*, *Hepatic pyrites*, or *Cellular pyrites*, which crystallises in trimetric forms. Cubic pyrites occurs abundantly in rocks of all ages, from the oldest crystalline to the most recent alluvial deposits, and has been found in small irregular crystals in the Vesuvian lavas. Marcasite occurs also in rocks of various ages, being found in granite, gneiss, and mica slate, and abundantly in the plastic clay of the brown coal formation near Carlsbad in Bohemia. The peculiar circumstances which determine the formation of one or other of these varieties are not known; neither has it been found possible to convert the one into the other. Iron pyrites is often formed from iron salts, in presence of putrefying organic matters, such as straw, wood, &c., the sulphide of iron thus produced retaining the form of the organic substance.

Yellow iron pyrites occurs in a great variety of monometric forms, the dominant forms being the cube, the octahedron, the trapezohedron 2O2 (*fig.* 180, ii. 125), the pentagonal dodecahedrons $\frac{2O\infty}{2}$ (*fig.* 192), and $\frac{\frac{3}{2}O\infty}{2}$, the hexakistetrahedrons $\frac{3O\frac{3}{2}}{2}$ and $\frac{4O2}{2}$ (hemihedral forms of the hexakis-octahedron, ii. 127), these forms occurring either alone or in combinations, such as *figs.* 194, 195, 196, 211, and numerous others. Twin-crystals are also found resulting from the intersection of two pentagonal dodecahedrons. Cleavage cubic and octahedral, more or less distinct; the cubic and octahedral faces are often striated. It likewise occurs radiated, subfibrous, and massive; often reniform or globular, with a crystalline surface. Hardness = 6 to 6·5. Specific gravity 4·083 to 5·031 (Dana); 5·0 to 5·2 (Rammelsberg). Lustre metallic, splendent; colour, bronze-yellow, nearly uniform. Streak, brownish black, opaque. Fracture conchoïdal, uneven. Brittle, strikes fire with steel. [For analyses, see p. 343.]

White iron pyrites or marcasite forms trimetric crystals, in which $a : b : c = 0·7454 : 1 : 1·1548$. Angle $\infty P : \infty P = 73° 24'$; $\breve{P}\infty : \breve{P}\infty$ in the basal principal section = 98° 13′. The crystals are pyramidal and prismatic combinations, the faces P∞ being frequently predominant in the latter. Cleavage tolerably distinct, parallel to ∞P. It occurs also in globular, reniform, and other imitative shapes; often massive, columnar, or granular. Hardness = 6 to 6·5. Specific gravity = 4·678 to 4·847 (Dana); 4·85 to 4·88 (Rammelsberg). Lustre metallic. Colour, pale bronze-yellow, sometimes inclining to green or grey. Streak, greyish-black or brown-black. Fracture uneven. Brittle.

Disulphide of iron is produced artificially: 1. By heating iron with excess of sulphur to a temperature below redness (Rammelsberg, Pogg. Ann. cxxi. 339).—2. By exposing ferric oxide or hydrate, ferroso-ferric hydrate, or ferrous carbonate, at a heat above 100°, but not amounting to redness, to a stream of sulphydric acid gas, as long as the mass continues to increase in weight. At first the action is so strong, that aqueous vapour, sulphurous anhydride, and hydrogen are evolved, and lower sulphides of iron are formed; but these afterwards take up more sulphur, and liberate pure hydrogen gas. The sulphide of iron thus produced retains the crystalline form of the oxide used in its preparation, with the same lustre on the faces, and the same directions of cleavage (Berzelius).—3. The lower sulphides of iron may be brought to this, the highest degree of sulphuration, by heating them in like manner in sulphydric acid gas (Berzelius).—4. An intimate mixture of 2 pts. protosulphide of iron and 1 pt. sulphur, heated in a retort to a temperature short of redness, leaves disulphide of iron as a bulky, dark yellow, non-magnetic, metallic powder, not attacked by hydrochloric acid (Berzelius).—5. When an intimate mixture of ferric oxide, sulphur, and sal-ammoniac is heated to a temperature a little above that at which the sal-ammoniac sublimes, the residue is found to contain small, brass-yellow octahedrons and cubes, which may be separated from the rest of the powder by levigation (Wöhler, Pogg. Ann. xxxvii. 238).—6. When sal-ammoniac containing sulphate of ammonium is sublimed at a dull red heat in iron vessels coated with clay, the clay covering becomes impregnated with chloride of iron, and cubes and octahedrons of iron pyrites form upon its surface (Löwe, *J. pr. Chem.* vi. 98).—7. The compound may also be prepared in the wet way by mixing solutions of alkaline persulphides with ferrous chloride at 180°, or ferrous sulphate at 165°. (Senarmont, Ann. Ch. Phys. [3] xxx. 129.)

Artificially prepared disulphide of iron differs in character according to the mode of preparation adopted, being either a bulky dark yellow powder (Berzelius), or crystallising in small brass-yellow cubes and octahedrons (Wöhler), or a black powder (Senarmont). It is not magnetic, is not attacked by dilute acids, but is decomposed by heating with strong hydrochloric acid, with evolution of sulphydric acid, and separation of sulphur, and is oxidised when heated with strong nitric acid or with nitro-muriatic acid.

Yellow iron pyrites in its compact forms, and the denser varieties of the artificial disulphide, do not alter by exposure to the air, and even that which is prepared in the wet way oxidises but slowly in the air, and only when moist; but white iron pyrites weathers very rapidly, and the yellow variety in the finely divided state oxidises even at ordinary temperatures, with sensible evolution of heat, as in the roasting of alum-stone, and the spontaneous heating of coal or lignite containing pyrites, which sometimes becomes intense enough to set fire to inflammable substances, and gives rise to the spontaneous combustion of coal-mines. The products of this spontaneous oxidation are, so long as the temperature remains moderate, sulphuric acid and ferrous sulphate, which separates partly in crystals, partly as an efflorescence on the surface, but is for the most part dissolved out by the water which permeates the mass (see SULPHATES); but at higher temperatures, sulphurous anhydride is evolved, and ferric oxide is left, with only a small quantity of sulphuric acid. This reaction renders iron pyrites available for the manufacture of sulphuric acid (*q. v.*). When ignited with charcoal, it yields sulphide of carbon. Mixed with 10 per cent. charcoal, and exposed to the action of a mixture of superheated steam and atmospheric air, it is completely desulphurised, giving off sulphur, sulphydric acid, and sulphurous anhydride, together with carbonic anhydride and carbonic oxide, while the iron remains, according to circumstances, either in the metallic state or as ferric oxide. (Brunfaut, Journ. des Mines, 1861, No. 5.)

IRON, TANTALATE OF. See TANTALITE.

IRON, TELLURIC. A term applied to native metallic iron found on the earth's surface, to distinguish it from meteoric iron.

IRON, TELLURIDE OF. See TELLURIDES.

IRON, TUNGSTATE OF. See TUNGSTATES.

ISAMIC ACID. $C^{16}H^{13}N^{3}O^{4}$. *Imasatic acid, Rubindenic acid.* (Laurent, Ann. Ch. Phys. [3] iii. 490.)—This acid is produced by the action of warm ammonia on isatin; but the best mode of preparing it is to dissolve isatin to saturation in aqueous potash; evaporate the solution to dryness; dissolve in alcohol; mix the solution with a very concentrated solution of sulphate of ammonium (in the proportion of rather more than 1 at. of that salt to 1 at. isatin); filter to separate sulphate of potassium; evaporate the filtered liquid to dryness, whereby the isatate of ammonium is converted into isamate; then boil with alcohol; filter to separate isamide and sulphate of ammonium; and neutralise the filtrate with hydrochloric acid, taking care to avoid an excess. Isamic acid then separates in crystals on cooling. If a small quantity of isatin should likewise separate, in consequence of too much hydrochloric acid having been added, or of too great a heat having been applied, or of the solution of isatate of ammonium not having been sufficiently evaporated, the crystals must be treated with weak ammonia, which dissolves the isamic acid and leaves the isatin.

Isamic acid crystallises in splendid, shining, rhombic laminæ, of the colour of red iodide of mercury. By spontaneous evaporation of the solution, ruby-coloured hexagonal tables are formed, with angles of about 110°. It dissolves sparingly in boiling water, forming a yellow solution, easily soluble in hot alcohol, somewhat less in ether.

Isamic acid dissolves with fine violet colour in hydrochloric acid. By boiling with dilute acids, it is converted into ammonia and isatin. Bromine attacks it violently, forming *indelibrome*, $C^{16}H^{6}Br^{6}N^{2}O^{3}$, a yellow substance insoluble in water.

Isamate of ammonium, $C^{16}H^{12}(NH^{4})N^{3}O^{4}$, crystallises in small needles or very acute microscopic rhombs. When somewhat strongly heated, it gives off water, and is converted into isamide. Its solution does not precipitate the salts of barium, calcium, or magnesium. It forms a yellow precipitate with *acetate of lead*, red with *mercuric chloride*, yellow with *nitrate of silver*.

Isamate of potassium may be boiled without decomposing.

Dichlorisamic acid, $C^{16}H^{11}Cl^{2}N^{3}O^{4}$.—Produced by adding hydrochloric acid to a solution of dichlorisamide in dilute potash, and crystallising the brick-red flocculent precipitate from alcohol. It forms bright red elongated hexagonal laminæ, derived from a rhombus of about 110°. It is more soluble than isamic acid in alcohol and ether, and forms yellow solutions. It is decomposed by distillation. Strong acids dissolve it, with violet colour, at ordinary temperatures; but at the boiling heat, they convert it into ammonia and chlorisatin.

Tetrachlorisamic acid, $C^{16}H^{9}Cl^{4}N^{3}O^{4}$.—Tetrachlorisamide is converted by boiling alcohol into tetrachlorisamate of ammonium; and on adding nitrate of silver to this salt, a flocculent precipitate is formed containing $C^{16}H^{8}AgCl^{4}N^{3}O^{4}$.

ISAMIDE. $C^{16}H^{14}N^{4}O^{3}$. *Amasatin*. (Laurent, Ann. Ch. Phys. [3] iii. 488.) Produced by heating isamate of ammonium till water is given off, and washing the residue with water. It is pulverulent, of a fine yellow colour, tasteless, inodorous, insoluble in water, nearly insoluble in ether, very sparingly soluble in alcohol, moderately soluble in boiling alcohol containing ammonia. Potash dissolves it with yellow colour, with elimination of ammonia; the solution contains isatin.

ISATAN. $C^{16}H^{12}N^{2}O^{3}$? (Laurent, J. pr. Chem. xxviii. 346.)—This body is sometimes produced when disulphisatyde is boiled with acid sulphite of ammonium, as a white precipitate, which dissolves when boiled with a large quantity of alcohol, and is deposited on cooling in crystals, which appear under the microscope, either as well-defined rectangles, or as pointed ovals, according to the side on which they are viewed. The compound, heated till it melts, turns brownish red, and yields a mixture of isatin and indin:

$$\underset{\text{Isatan.}}{3C^{16}H^{12}N^{2}O^{3}} = \underset{\text{Isatin.}}{2C^{8}H^{5}NO^{2}} + \underset{\text{Indin.}}{2C^{16}H^{12}N^{2}O^{2}} + H^{2}O.$$

It is decomposed by boiling nitric acid, with formation of a violet powder, similar to nitrindin. With alcoholic potash it forms a yellow solution, from which water precipitates hydrindin, and hydrochloric acid throws down isatin mixed with a resinous substance.

The composition of isatan is equal to that of 2 at. indigo-blue + 1 at. water ($2C^{8}H^{5}NO + H^{2}O$), and to that of isatyde *minus* 1 at. oxygen ($C^{16}H^{12}N^{2}O^{4} - O$).

ISATIC ACID. $C^{8}H^{7}NO^{3}$. (Laurent, Ann. Ch. Phys. [3] iii. 371.)—The potassium-salt of this acid is produced by the action of caustic potash upon isatin. The acid itself is not easily obtained in the free state.

The solution of the potassium-salt mixed with hydrochloric acid, deposits, after a while, crystals of isatin, which in fact differs from isatic acid, only by the elements of water:

$$\underset{\text{Isatic acid.}}{C^{8}H^{7}NO^{3}} = \underset{\text{Isatin}}{C^{8}H^{5}NO^{2}} + H^{2}O.$$

The composition of the isatates is represented by the formula $C^{8}H^{6}MNO^{3}$. The ammonium-salt appears to be capable of existing only in solution; for on evaporation to dryness, it gives off water, and is converted into isamate of ammonium (p. 404). The *barium-salt*, $C^8H^6BaNO^3$, produced by the action of baryta-water on isatin, crystallises in scales. The *potassium-salt* contains $C^8H^6KNO^3$. Isatin dissolves in a cold strong solution of potash, forming a deep violet-red liquid, which changes to pale-yellow when diluted with water and boiled. On evaporating the solution, the salt is obtained in crystals of a faint yellow colour. It precipitates chloride of barium if the solutions are concentrated, and forms with acetate of lead, a yellow flocculent precipitate, which gradually turns red. The *silver-salt*, $C^8H^6AgNO^3$, is soluble in water, and crystallises in beautiful yellow prisms. It is obtained as a precipitate on mixing the boiling and rather concentrated solutions of isatate of potassium and nitrate of silver.

Bromisatic acid, $C^8H^6BrNO^3$, is obtained as a potassium-salt by the action of cold aqueous potash on bromisatin.

Dibromisatic acid, $C^8H^5Br^2NO^3$. (Erdmann, J. pr. Chem. xix. 360.)—This acid is obtained, by adding hydrochloric acid to a concentrated solution of its potassium-salt, as a light yellow pulverulent substance, soluble in a larger quantity of water. By desiccation, even in vacuo, at mean temperatures, it is converted into dibromisatin.

Dibromisate of potassium, $C^8H^4KBr^2NO^3.H^2O$, is prepared by dissolving dibromisatin in cold aqueous potash, and leaving the solution to itself for a while. It crystallises in pale yellow, shining needles, less soluble in water and in alcohol than the dichlorisatate. It gives with metallic salts the same reactions as the dichlorisatate. *Sulphurous acid* converts it into *dibromisatosulphite of potassium*, $C^8H^4KBr^2NO^3.2SO^2$.

Chlorisatic acid. $C^8H^6ClNO^3$. (Erdmann, Ann. Ch. Pharm. xxxiii. 129.—Laurent, Ann. Ch. Phys. [3] iii. 378.)—This acid is not known in the free state, but several of its salts have been prepared.

Chlorisatate of potassium, $C^8H^5KClNO^3$, is obtained by mixing warm, moderately concentrated solutions of caustic potash and chlorisatin. The salt separates on cooling and may be purified by repeated crystallisation from alcohol. It crystallises in shining flattened quadrilateral needles of a light yellow colour, soluble in water and alcohol, and decomposed by heat. Hydrochloric acid added to its solution throws down chlorisatin.

The other salts of chlorisatic acid are obtained by double decomposition. The *barium-salt* separates on cooling from a mixture of the hot solutions of chlorisatate of potassium and chloride of barium, sometimes in pale yellow needles containing $2C^8H^5BaClNO^3.H^2O$, sometimes in deep yellow, very brilliant laminæ containing $2C^8H^5BaClNO^3.3H^2O$. Both these hydrates give off their water between 150° and 160°. The *bismuth-salt* has a deep orange-yellow colour. The *calcium-salt* resembles the barium-salt. The *cadmium-salt* is yellow. The *cupric salt*, when first precipitated, is bulky, and of the colour of ferric hydrate, but changes after a while to a heavy granular powder of a blood-red colour. The *ferric salt* is a brown-red precipitate obtained by adding chlorisatate of potassium to iron-alum. The *lead-salt*, $C^8H^5PbClNO^3.H^2O$, is produced as a brilliant yellow gelatinous precipitate, which, in a few minutes, especially if agitated, becomes flocculent, and of a splendid scarlet colour, almost as bright as that of mercuric iodide. Under the microscope, the yellow precipitate appears pulverulent, without any trace of crystallisation, but the red flocks present the appearance of dendritic vegetation. These red flocks contain 1 at. water, which they give off at 160°. The *magnesium-* and *aluminium-salts* appear to be soluble. The *mercury-salts* are yellow precipitates. The *nickel-salt* is a yellowish crystalline powder. The *silver-salt*, $C^8H^5AgClNO^3$, is a light yellow precipitate, which dissolves in boiling water and crystallises on cooling in needles grouped in tufts, or in dendritic vegetations of yellowish colour. The *zinc-salt* is a yellow precipitate.

Dichlorisatic acid. $C^8H^5Cl^2NO^3$. (Erdmann, Laurent, *loc. cit.*)—This acid separates from a concentrated solution of its potassium-salt, on addition of a mineral acid, in the form of a yellow precipitate, which, however, cannot be obtained pure; for by desiccation, even in vacuo at mean temperature, it separates into dichlorisatin and water. It dissolves in water, forming a light yellow solution, which becomes turbid at 60°, and deposits dichlorisatin.

Dichlorisatate of potassium, $C^8H^4KCl^2NO^3.H^2O$.—Dichlorisatin dissolves in cold aqueous potash, forming a deep red solution which becomes colourless when heated, and on cooling deposits the potassium-salt in shining yellow laminæ, which may be purified by crystallisation from alcohol. They contain I at. water (= 5 per cent.), which is not completely expelled below 130°. When crystallised from absolute alcohol, the salt appears to contain only half of that quantity of water. It is decomposed by heat, with a kind of explosion.

The *barium-salt*, $C^8H^4BaCl^2NO^3.H^2O$, forms shining golden-yellow needles.—The *cupric salt* is a red-brown precipitate, which soon becomes greenish yellow and alternately crimson, these changes of colour arising from the crystallisation of the salt within the liquid. The *lead-salt* is a yellow precipitate. The *silver-salt* is a light yellow precipitate, which dissolves in a large quantity of boiling water, and crystallises on cooling in transparent yellowish needles, grouped in tufts. When heated in contact with the air, it melts to a brown mass, and yields a sublimate of dichlorisatin.

ISATILIM. $C^{24}H^{16}N^4O^5$ = 3 at. isatin + NH^3 − H^2O.—A substance stated by Laurent (J. pr. Chem. xxxv. 121) to be sometimes obtained when dry ammonia-gas is passed over isatin moistened with alcohol. Yellow non-crystalline flocks easily decomposed by potash. Its composition is rather doubtful.

ISATIMIDE. $C^{24}H^{17}N^5O^4$. (Laurent, *loc. cit.*)—Obtained by passing dry ammonia-gas over isatin moistened with alcohol, either ordinary or absolute. When absolute alcohol is used, *imesatin* (p. 246) first crystallises out in prisms with square or rectangular base; and the solution decanted therefrom deposits isatimide in the form of a yellow, shining, crystalline powder. It is insoluble in water, scarcely soluble in boiling alcohol or in ether, but dissolves easily in boiling alcohol, containing ammonia. Potash dissolves it with yellow colour and evolution of ammonia; the liquid contains isatin.

ISATIN. $C^8H^5NO^2$. (Laurent, Ann. Ch. Phys. [3] iii. 371.—Erdmann, J. pr. Chem. xxiv. 11.—A. W. Hofmann, Ann. Ch. Pharm. liii. 11.—Gm. xii. 51.—Gerh. iii. 534.)—This body, which was discovered simultaneously by Laurent and by Erdmann, in 1841, is produced by the action of nitric or chromic acid upon indigo:

$$\underset{\text{Indigo.}}{C^8H^5NO} + O = \underset{\text{Isatin.}}{C^8H^5NO^2}.$$

Preparation.—1 kilogramme of finely powdered, good commercial indigo is stirred up in a large dish to a thin paste with water; it is then placed over a moderate fire, and commercial nitric acid is gradually added (which causes a violent effervescence, without evolution of nitrous acid), until the blue colour has disappeared, for which, from 600 to 700 grms. of nitric acid are necessary. The solution is boiled with several quarts of water, and filtered at the boiling heat, as rapidly as possible; after 12 hours, the isatin separates in reddish crystalline nodules. The mother-liquor is boiled with the undissolved residue and filtered, the operation being two or three times repeated: the last mother-liquor still yields isatin on evaporation. The crystals are moistened with water containing a little ammonia, in order to remove a resinous matter; they are then washed with cold water, and finally recrystallised several times from boiling alcohol (100 pts. of indigo yield 18 pts. of isatin) (Laurent). When an excess of nitric acid is employed, nitrosalicylic acid is formed. After each addition of nitric acid, it is necessary to wait until the effervescence is over. If no effervescence takes place, in consequence of the indigo being mixed with too much water, and if the boiling is continued, whilst more and more nitric acid is added, a violent reaction suddenly ensues when the solution has reached a certain concentration, the mass overflowing the vessel even when it is very capacious: the residue generally contains nitrosalicylic acid (Hofmann).—2. Indigo is heated with chromic acid, properly diluted, until the whole nearly boils, when it is filtered hot; isatin then crystallises out on cooling, and is purified by repeated recrystallisation from water, and lastly from alcohol. If the chromic acid is so concentrated that it causes an evolution of carbonic anhydride, the solution deposits little or no isatin on cooling, but a small quantity by spontaneous evaporation or in vacuo; on evaporating the solution by heat, only sesquioxide of chromium and a brown powder separate (Erdmann). Laurent drops a dilute aqueous solution of chromic acid upon powdered indigo, and warms the mixture, the addition of chromic acid being discontinued as soon as the blue colour has disappeared, and the process continued as in (1). In order to purify crude isatin, which still contains resin, Hofmann dissolves it in potash, and carefully adds hydrochloric acid to the solution, as long as it forms a black or brown precipitate; when a portion on filtering is of a pure yellow colour, and gives a highly red precipitate with hydrochloric acid, the whole solution is filtered off, decomposed with hydrochloric acid, and the precipitate washed with a little water.

Properties.—Isatin crystallises in large, transparent, brownish-red prisms, or in smaller yellowish-red prisms, belonging to the trimetric system; the crystals are very brilliant, especially when obtained from an alcoholic solution. They exhibit the combination $\infty P . \infty \breve{P}\infty . \breve{P}\infty$; the faces $\infty \breve{P}\infty$ greatly predominating. Inclination of the faces $\infty P : \infty P$ = 133° 50′ to 133° 55′; $\breve{P}\infty : \breve{P}\infty$ = 127° 15′ to 127° 30′ (G. Rose, J. pr. Chem. xxiv. 11). Isatin is inodorous, and has a bitter taste. It melts when heated, and solidifies on cooling in a crystalline mass of needles; when heated above its melting point in contact with the air, the greater part volatilises, without decome position, in yellow and very irritating vapours. It dissolves sparingly in cold, mor- freely in boiling *water*, forming a solution of a dark-reddish yellow colour. *Nitric* *acid* dissolves it with the aid of a gentle heat, and deposits it unchanged on cooling. It dissolves readily in *alcohol*, less easily in *ether*.

Decompositions.—Isatin distilled in a retort leaves a large residue of charcoal (Erdmann, Laurent). When thrown upon glowing charcoal, it diffuses the same odour as indigo. Heated in the air upon platinum-foil, it burns with a brilliant flame, and leaves a fused residue of difficultly combustible charcoal.—2. When isatin is suspended in hot water, and a current of *chlorine* is passed through the solution, it is converted into chlorisatin; no dichlorisatin is formed, even if the solution is exposed to sunshine.—3. Isatin heated to 180° with *chloride of benzoyl*, yields a brown substance having the composition of benzoyl-isatin, $C^8H^4(C^7H^5O)NO^2$.—4. Moderately warm *nitric acid* dissolves isatin without decomposition, but on boiling, a violent action takes place, attended with evolution of nitrous fumes, oxalic acid being formed together with a reddish-brown nitro-resin, soluble in ammonia; no picric acid is formed.—5. Isatin heated with *fuming sulphuric acid*, dissolves with brownish-red colour; a strong effervescence then takes place, and on treating the solution with water and alcohol, a yellow substance is obtained, which has not been further investigated.—6. Isatin dissolves in cold *potash* without undergoing decomposition, and imparts to it a brownish red colour: after a time, or immediately on boiling, the solution becomes yellow and is found to contain isatate of potassium:

$$C^8NH^5O^2 + H^2O = C^8NH^7O^3.$$

If this solution be concentrated by distillation, decomposition suddenly takes place, colourless drops of phenylamine passing over with the steam, and hydrogen being simultaneously evolved (Hofmann):

$$C^8H^5NO^2 + 4KHO = C^6H^7N + 2K^2CO^3 + H^2.$$

7. *Ammonia* forms with solutions of isatin, various products of decomposition, which vary according to the concentration of the ammonia and the solvent of the isatin; mixtures of several compounds are always formed, each containing 1, 2, or 3 at. isatin, *plus* 1 or 2 at. ammonia *minus* water.—8. *Phenylamine* behaves with isatin in a similar mannner.—9. With *sulphurous acid* in presence of alkalis, isatin forms salts of isatosulphurous acid.—It dissolves in *sulphite of ammonium*, with formation of isatyde.—10. When *sulphydric acid gas* is passed through an alcoholic solution of isatin, disulphisatyde (p. 412) is formed.

Isatites.—Isatin does not unite with acids, but rather itself plays the part of an acid, exchanging 1 at. of its hydrogen for an equivalent quantity of metal. Isatin dissolves in cold strong aqueous potash, forming a very dark violet-red liquid, probably containing *isatite of potassium*, $C^8H^4KNO^2$. On diluting with water and boiling, the colour changes to pale yellow, and the solution is then found to contain isatate of potassium. *Isatite of cuprammonium*, $C^8H^4(NH^2Cu)NO^2$, is obtained as a light blue precipitate on pouring an ammoniacal solution of isatin into an ammoniacal solution of acetate of copper. *Isatite of silver*, $C^8H^4AgNO^2$, is a wine-red crystalline precipitate, obtained by mixing nitrate of silver with an alcoholic solution of isatin. It gave by analysis 42·5 and 42·2 per cent. silver (calculated quantity 42·52). On adding nitrate of silver to an alcoholic solution of iodine containing a considerable quantity of ammonia, a red crystalline precipitate is formed, consisting of *isatite of argentammonium*, $C^8H^4(NH^2Ag)NO^2$. It gave by analysis 35·23 per cent. carbon, 2·66 hydrogen, and 39·75 silver (by calculation, 35·42 carbon, 2·58 hydrogen, and 39·85 silver).

Brominated and Chlorinated Derivatives of Isatin.

These compounds, which were discovered by Erdmann, have the composition of isatin, in which 1 or 2 at. hydrogen are replaced by an equivalent quantity of bromine or chlorine. They closely resemble isatin in form and properties, and when treated with caustic potash, ammonia, sulphydric acid, or alkaline sulphites, yield the chlorinated and brominated derivatives of the bodies which are produced by the action of the same reagents upon isatin.

Bromisatin. $C^8H^4BrNO^2$. (Erdmann, J. pr. Chem. xix. 358.—Hofmann, Ann. Ch. Pharm. liii. 40.)—This compound is produced, together with dibromisatin, by the action of bromine upon indigo. The product is exhausted with boiling water, and the crystals which separate on cooling, are purified by recrystallisation from alcohol, the first portions which separate consisting principally of bromisatin (Erdmann). Another mode of preparation is to suspend isatin in water, and shake it up in sunshine with bromine, which is to be gradually added till the liquid no longer becomes colourless on agitation. The compound is then boiled with weak alcohol, freed from hydrobromic acid by washing with water, and recrystallised from boiling alcohol. (Hofmann.)

Bromisatin crystallises by cooling in shining orange-coloured prisms. Caustic potash converts it, at mean temperatures, into bromisatate of potassium. Distilled with hydrate of potassium, it yields bromophenylamine.

Dibromisatin. $C^8H^3Br^2NO^2$. (Erdmann, *loc. cit.*—Hofmann, *loc. cit.*—Laurent, Ann. Ch. Phys. [3] iii. 380.)—This body remains in the alcoholic mother-liquors obtained in preparing bromisatin, by the first of the methods above described, and may be separated by crystallisation; but a better way of preparing it is to digest isatin or bromisatin with bromine in sunshine, as long as hydrobromic acid continues to escape. It is purified by crystallisation from alcohol, from which it separates in shining orange-coloured trimetric prisms. When distilled with hydrate of potassium, it yields dibromophenylamine.

Dibromisatite of potassium, $C^8H^2KBr^2NO^2$, is obtained by gently heating a solution of dibromisatin in absolute alcohol, and pouring into it a hot solution of alcoholic potash. It crystallises in black scales, blue by transmitted light.

Chlorisatin. $C^8H^4ClNO^2$. (Erdmann, Ann. Ch. Pharm. xxiii. 129.—Laurent, Ann. Ch. Phys. [3] iii. 478.—Hofmann, Ann. Ch. Pharm. liii. 12.)—Produced: 1. By passing chlorine into tepid water, in which isatin is suspended.—2. By the action of chlorine on pulverised indigo suspended in water. A large quantity of a reddish yellow substance is thereby produced, consisting of a mixture of chlorisatin and dichlorisatin, which may be separated by solution in boiling alcohol, the chlorisatin separating out first. It is purified by repeated crystallisation from alcohol.

Chlorisatin crystallises in orange-coloured prisms, isomorphous with isatin. Observed combination, $\infty P \,.\, \infty\breve{P}\infty \,.\, \breve{P}\infty$. Inclination of the faces, $\infty P : \infty P = 131°$; $\breve{P}\infty : \breve{P}\infty = 134° 12'$ (G. Rose). It is inodorous, but has a bitter taste. Its dust irritates the organs of respiration and provokes sneezing. It is insoluble in cold water, but dissolves readily in boiling water and in alcohol. The solutions impart a disagreeable odour to the skin. Heated in contact with the air, it melts to a brown liquid, and gives off yellow vapours having the odour of burning indigo. At a high temperature, it partly sublimes and is partly carbonised.

Chlorisatin behaves with reagents like isatin. It dissolves in strong *sulphuric acid*, and separates on addition of water. With *nitric acid* it yields a resinous substance, oxalic acid, and a small quantity of an azotised body, which crystallises in yellow grains. *Sulphydric acid gas* passed into an alcoholic solution of chlorisatin, forms a white precipitate which increases on addition of water. Erdmann calls this precipitate sulphochlorisatin; according to Gerhardt, it is perhaps chlorinated tetrasulphisatyde, $C^{16}H^{10}Cl^2N^2S^4$ (analysis, 41·7 C, 2·37 H, and 31·09 S; calculation, 44·7 C, 2·33 H, 29 83 S).

Caustic *potash* communicates a deeper colour to chlorisatin, converting it into chlorisatite of potassium; on heating the liquid, the colour disappears, and the liquid contains chlorisatate of potassium.

Chlorisatite of argentammonium, $C^8H^3(NH^3Ag)ClNO^2$, is a crystalline precipitate, of the colour of wine-lees, obtained by pouring an ammoniacal solution of nitrate of silver into an alcoholic solution of chlorisatin mixed with ammonia.

Dichlorisatin, $C^8H^3Cl^2NO^2$, is obtained from the alcoholic mother-liquors, which have yielded chlorisatin, and is purified by recrystallisation from alcohol. It crystallises in small shining reddish-yellow needles, or shortened laminæ, fusible, partly volatile when heated in a close vessel, soluble in water and in alcohol.

Aqueous *potash* acts upon it in the same manner as upon chlorisatin. When dichlorisatin is thrown upon solid potash moistened with absolute alcohol, a red solution is formed, which after a short time, solidifies in a violet-black magma composed of dichlorisatite of potassium, the solution of which forms with nitrate of silver a precipitate having the colour of wine-lees.

Chlorine does not act upon chlorisatin or dichlorisatin in presence of water, but when either of these bodies is dissolved in hot alcohol of 80 per cent., and chlorine gas is passed through the liquid until nothing is formed but products of the decomposition of alcohol, a brownish yellow viscid mass is deposited at the bottom of the vessel, containing shining laminæ of *perchloroquinone* (chloranil). Water extracts salammoniac from this mass, and alcohol dissolves chloride of ethyl, pentachloropicric acid, and a resinous mass which forms the largest portion of the product. The supernatant yellow solution contains products of the action of chlorine upon alcohol, and yields by distillation, a residue corresponding to the resinous substance, but not containing perchloroquinone. (Erdmann, Hofmann.)

ISATOSULPHURIC ACIDS. (G. and A. Schlieper, Ann. Ch. Pharm. cxxi. 1.)—Sulphindigotic acid, treated with oxidising agents, such as nitric acid or chromic acid, yields a monobasic acid containing the elements of isatin and sulphuric anhydride, viz. $C^8H^5NO^2.SO^3$; and the salts of this acid, treated with alkalis, yield a dibasic acid, containing the elements of isatin and sulphuric acid, viz. $C^8H^5NO^2.SO^4H^2$.

To prepare the monobasic acid, a superior sort of commercial indigo-carmine (p. 261) is stirred up to a thin paste with an equal quantity of water; 1 or 2 pts. of sulphuric acid are added; the mass is heated to boiling; and 1 pt. of pulverised acid chromate of potassium is added by small portions as long as decoloration ensues. The solution is then quickly filtered while hot, and mixed with nitrate of potassium (to facilitate the solution of the isatosulphate); the crystalline paste which separates is collected on a filter; and the thick, dark-coloured mother-liquor is separated by displacement with a small quantity of water. This liquid, evaporated and cooled, yields a small additional quantity of the potassium-salt. The isatosulphate of potassium thus obtained, in the form of a brownish yellow, heavy, sandy powder, is contaminated with a resinous body, which adheres to it obstinately, and cannot be separated. The acid and its salts may, however, be obtained pure by converting them into dibasic isatosulphates by the action of alkalis, and reconverting these into the monobasic isatosulphates with acids. The impure potassium-salt obtained as above is dissolved in hot baryta-water, which is added till the solution is completely decolorised, and the excess of baryta is precipitated by carbonic acid, the precipitate carrying down all the resinous impurities with it. The resulting pale straw-yellow solution contains a mixture of dibasic isatosulphate of potassium and dibasic isatosulphate of barium; and on precipitating the baryta as exactly as possible with sulphuric acid, an orange-yellow solution of the monobasic salt is obtained, whence the salt may be separated by evaporation and crystallisation. If on the other hand, the solution be saturated while hot, with a quantity of hydrochloric acid just sufficient to neutralise the potash, the liquid, which has now acquired a dark orange colour, deposits bulky, bright red, shining crystalline scales of monobasic isatosulphate of barium.

Monobasic Isatosulphuric acid, $C^8H^5NSO^5.2H^2O = C^8H^5NO^2.SO^3.2H^2O$, may be obtained in the free state by decomposing the solution of the barium-salt with an equivalent quantity of sulphuric acid.

The resulting orange-red, strongly acid solution, solidifies, when evaporated to a syrup, into a somewhat sticky, radio-crystalline mass, drying up in vacuo over sulphuric acid to a yellow, silky crystalline mass, which does not alter on exposure to the air at common temperatures. but easily gives up its water of crystallisation at 100°. It dissolves in *alcohol* less easily than in water, and is insoluble in *ether* and in *benzene*.

Isatosulphuric acid is a strong acid, separating even the stronger mineral acids from their salts. It is not decomposed by strong *sulphuric* or *nitric acid*, even with the aid of heat; but *nitromuriatic acid*, or a mixture of *hydrochloric acid* and *chlorate of potassium* slowly decomposes it, with formation of chloranil. The aqueous solution appears to be scarcely altered by *chlorine*. The alcoholic solution treated with *ammonia gas* yields viscid, dark brown-red bodies, probably amidated compounds. The acid is not reduced by *hydriodic acid*, but the reduction is effected by *zinc* and *hydrochloric* or *sulphuric acid*, the solution being thereby completely decolorised. *Sulphydric acid*, and especially *sulphide of ammonium*, likewise reduce the acid, yielding the ammonium-salt of hydrindin-sulphuric acid (p. 266).

Salts of Monobasic Isatosulphuric acid.—*Mono-ammonic isatosulphate*, $C^8H^4(NH^4)NSO^5.H^2O$, is obtained by decomposing any other salt of the acid with an excess of an ammonium-salt in which the resulting salt is sparingly soluble; or by mixing a solution of the free acid with excess of sal-ammoniac. The salt crystallises in shining, deep yellow needles, easily soluble in water.

The *monobarytic salt*, $C^8H^4BaNSO^4.\frac{1}{2}H^2O$, is formed by precipitating a solution of chloride or nitrate of barium with the free acid. It is insoluble in alcohol, sparingly soluble in cold, somewhat more in hot water, forming a light yellow solution.

The *monocalcic salt*, $C^8H^4CaSO^5.H^2O$, is obtained by precipitation, and crystallises in small, shining, gold-yellow needles which dissolve somewhat slowly in water, but more easily than the barium-salt.

The *monopotassic salt*, $C^8H^4KNSO^5.H^2O$, crystallises in small gold-yellow needles which yield a sandy powder. It is insoluble in alcohol, dissolves in about 20 pts. of cold, and somewhat less of hot water, whence it crystallises slowly. It is not altered by boiling with strong hydrochloric acid. It gives off all its water of crystallisation at a rather high temperature; indeed all the salts of monobasic isatosulphuric acid retain their water till heated above 100°.

The *mono-argentic salt*, $C^8H^4AgNSO^5.H^2O$, separates slowly on mixing a solution of the sodium-salt with nitrate of silver, in hard, needle-shaped, honey-yellow crystals, sparingly soluble in water.

The *monosodic salt*, $C^8H^4NaNSO^5.2H^2O$, is obtained by mixing a hot-saturated solution of the potassium-salt with two or three times its volume of a concentrated solution of chloride of sodium, and crystallises, on leaving the liquid at rest, in deep red tabular crystals.

Salts of Dibasic Isatosulphuric acid, $C^8H^3M^2NSO^6 = C^8H^5NO^4.SO^4M^2$.

These salts are formed, as already observed, by the action of alkalis on the monobasic isatosulphates. All alkalis produce the change provided they are added in excess; if an insufficient quantity of alkali be added, a deep red, or sometimes dirty violet colouring is produced, which, though transient, is sufficient to indicate the formation of an intermediate compound. The transformation is likewise effected by alkaline carbonates.

Dibasic isatosulphuric acid has not been isolated; when separated from the solution of either of its salts, it is converted in a short time at ordinary temperatures, immediately when heated, into the monobasic acid.

The *diammonic salt* is produced by boiling isatosulphuric acid for some time with excess of ammonia, or by decomposing the dibarytic salt with sulphate of ammonium. The solution dries up, in vacuo over oil of vitriol, to a yellow gummy mass exhibiting but slight traces of crystallisation.

The *dibarytic salt*, $C^8H^5Ba^2NSO^6 . 3H^2O$, is obtained by dissolving the monobarytic salt in boiling baryta-water, and removing the excess of baryta with carbonic acid. The slightly coloured solution yields, by evaporation or cooling, shining, lemon-yellow silky needles, more soluble than the monobasic salt in water, but insoluble in alcohol.

The *diplumbic salt*. $C^8H^5Pb^2NSO^6 . \frac{2}{3}H^2O$, is obtained by mixing a concentrated solution of the yellow potassium-salt with an excess of a concentrated solution of acetate of lead; it crystallises in slender, shining, dark yellow needles, which dissolve readily in water.

The *dipotassic salt*, $C^8H^5K^2N^2SO^6 . H^2O$, obtained by decomposing the barium-salt with neutral sulphate of potassium, crystallises slowly, by spontaneous evaporation, in hard, shining, transparent, wax-yellow prisms, which dissolve readily in water, and give off their water of crystallisation between 140° and 150°.

The *diargentic acid*, $C^8H^5Ag^2NSO^6 . \frac{2}{3}H^2O$, separates on mixing a solution of the potassium-salt with excess of nitrate of silver, in concentric groups of bulky needles, which, after drying, form a light spongy pale yellow mass. It is sparingly soluble in water, and does not give off its water of crystallisation till heated above 100°.

ISATOSULPHITES. (Laurent, Rev. scient. x. 289.—Gm. xiii. 56.—Gerh. iii. 544.)—Sulphurous anhydride does not act upon isatin alone; but in presence of potash or ammonia, peculiar salts are produced, containing the elements of isatate of ammonium or potassium, together with sulphurous anhydride. The acid corresponding to these salts has not been isolated, being decomposed when the salts are treated with a stronger acid. The chlorinated and brominated isatins yield corresponding compounds under the influence of alkalis and sulphurous acid.

Isatosulphite of Ammonium, $C^8H^6(NH^4)NO^3.2SO^2$, is obtained by boiling isatin with acid sulphite of ammonium, and concentrating the liquid by evaporation. It then separates in small rhomboïdal tables of a pale yellow colour, sparingly soluble in cold, but very soluble in boiling water.

Isatosulphite of Potassium, $C^8H^6KNO^3.2SO^2$, is produced by passing sulphurous anhydride to saturation into a solution of isatin in potash, or into a solution of isatate of potassium, or by boiling powdered isatin with acid sulphite of potassium, till it is completely dissolved.

The salt is neutral, has a faint yellow colour, is moderately soluble in water, and crystallises therefrom in elongated laminæ possessing considerable lustre. It is moderately soluble in boiling alcohol, very little in cold alcohol. Its solutions are yellow. When heated it aquires an orange-red colour, swells up and gives off water, and at a higher temperature blackens, and gives off a red thick matter, which solidifies without crystallising.—Iodine decomposes it at the boiling heat, isatin being precipitated and sulphuric acid remaining in the liquid. Chlorine also forms sulphuric acid, but at the same time throws down chlorisatin or dichlorisatin, according to the duration of the action. Hydrochloric acid poured into a boiling solution of the salt eliminates sulphurous anhydride, with effervescence, and precipitates isatin.

The solution of the potassium-salt does not form any precipitate with chloride of barium, strontium, or calcium, or with acetate of copper; but with nitrate of silver and acetate of lead, it forms precipitates consisting of a metallic sulphite, together with isatin.

Dibromisatosulphite of Potassium, $C^8H^4Br^2KNO^3.2SO^2$, is a yellow precipitate, sparingly soluble in water.

Chlorisatosulphite of Potassium, $C^8H^5ClKNO^3.2SO^2$, is obtained by passing sulphurous anhydride into a solution of chlorisatate of potassium. The liquid yields by evaporation a straw-yellow, fibro-lamellar salt, sparingly soluble in cold water. Acids decompose it, with precipitation of chlorisatin and evolution of sulphurous anhydride.

Dichlorisatosulphite of Potassium, $C^8H^4Cl^2KNO^3.2SO^2$. Yellow needles obtained by boiling dichlorisatin with acid sulphite of potassium.

ISATYDE. $C^{16}H^{12}N^2O^4 = (C^8H^5NO^2)^2.H^2$. (Laurent, Ann. Ch. Phys. [3] iii. 382.—Gm. xiii. 98.—Gerh. iii. 551.)—A substance produced by the action of reducing agents, such as nascent hydrogen, sulphydric acid, sulphide of ammonium, &c. on isatin; *e.g.:*

$$\underset{\text{Isatin.}}{2C^8H^5NO^2} + H^2S = \underset{\text{Isatyde.}}{(C^8H^5NO^2)^2.H^2} + S.$$

It bears to isatin the same relation that indigo-white bears to indigo-blue.

The best mode of preparing it is to mix powdered isatin in a flask with a large quantity of water and a little sulphuric acid, then add a piece of pure zinc-foil, and heat the liquid. As the isatin dissolves, it takes up the nascent hydrogen, and is converted into pulverulent isatyde, which may be washed with water, and then boiled with alcohol to remove undecomposed isatin. Isatyde may likewise be obtained by dissolving isatin in hot alcohol, and adding a small quantity of sulphide of ammonium. The mixture left to itself for a week deposits laminated and prismatic crystals of isatyde, mixed with octahedral crystals of sulphur, which must be removed by digestion with disulphide of carbon.

Isatyde is white, with a slight greyish tint, tasteless, and inodorous, and appears to be insoluble in water. It dissolves in very small quantity, in alcohol and ether, at the boiling heat, and separates on cooling in microscopic scales, having the form of oblique prisms with rectangular base.

Isatyde softens when heated, and then turns violet-brown (being perhaps converted into a mixture of indin and isatin); if the heat be increased till the body is half melted, it suffers further decomposition, yielding a substance which dissolves in alcohol and crystallises in brown-red needles by evaporation.

Boiling nitric acid decomposes isatyde, producing a violet powder which ultimately dissolves. Potash likewise decomposes it, forming isatate of potassium and indin-potassium, which ultimately changes to hydrindin-potassium and other products of unknown constitution (see p. 264).

Erdmann (J. pr. Chem. xxiv. 15) gives the name of *isatyde* to a substance which he obtained by dissolving isatin in hot sulphide of ammonium. This substance gave by analysis numbers agreeing approximately with the formula $C^{16}H^{12}N^2O^6$. It was white, very slightly crystalline, scarcely soluble in water, but soluble in ammonia, with red colour gradually changing to yellow. Potash dissolved it with deep-red colour, disappearing when the liquid was heated; the solution, on cooling, deposited a crystalline salt, and yielded yellow flocks with hydrochloric acid.

Chlorisatydes and **Bromisatydes.** (Erdmann, Ann. Ch. Pharm. xxxiii. 129.—Laurent, Ann. Ch. Phys. [3] iii. 382.)—*Dichlorisatyde*, $C^{16}H^{10}Cl^2N^2O^4$, is produced by the action of sulphide of ammonium on chlorisatin. It is white, crystallisable, insoluble in cold water, sparingly soluble in hot water; moderately soluble in boiling alcohol, soluble also, apparently without alteration, in a hot solution of sulphide of potassium. Heated to 180°, it is resolved into chlorisatin and chlorindin:

$$\underset{\text{Chlorisatyde.}}{2C^{16}H^{10}Cl^2N^2O^4} = \underset{\text{Chlorindin.}}{C^{16}H^8Cl^2N^2O^2} + \underset{\text{Chlorisatin.}}{2C^8H^4ClNO^2} + 2H^2O$$

Chlorisatyde is coloured red by *ammonia*, and partially dissolved. It dissolves in boiling aqueous *potash*, being converted into chlorisatate of potassium, which crystallises on cooling. The mother-liquor, treated with *hydrochloric acid*, yields a copious light-yellow precipitate, which is partially dissolved by boiling water, the insoluble part consisting of chlorindin, and the dissolved portion of chlorisatydic acid, probably a product of the decomposition of chlorindin. This acid is deposited from the aqueous solution in the form of a lemon-yellow substance, which forms, with potash, a soluble salt having little tendency to crystallise. The solution gives, with salts of lead, copper and barium, yellow precipitates which redissolve in the liquid when heated.

Tetrachlorisatyde, $C^{16}H^8Cl^4N^2O^2$.—Produced by the action of sulphide of ammonium on tetrachlorisatin. It resembles the preceding compound, and is decomposed in like manner by heat into tetrachlorisatin and tetrachlorindin. It likewise behaves in a similar manner when boiled with potash, yielding, among other products, probably by a secondary decomposition of dichlorindin, the potassium-salt of a peculiar acid (*dichlorisatydic* acid) which, as the liquid cools, is deposited in yellow, shining laminæ.

Tetrabromisatyde, $C^{16}H^8Br^4N^2O^2$, resembles tetrachlorisatyde, and is prepared in a similar manner. It turns brown when heated, and is resolved into dibromisatin and dibromindin.

Sulphisatyde, $C^{16}H^{12}N^2O^2S$. *Sulphasathyde.* (Laurent, Ann. Ch. Phys. [3]

iii. 463).—Obtained by adding alcoholic potash drop by drop to an alcoholic solution of disulphisatyde:

$$\underset{\text{Disulphisatyde.}}{C^{16}H^{12}N^{2}O^{2}S^{2}} + KHO = \underset{\text{Sulphisatyde.}}{C^{16}H^{12}N^{2}O^{3}S} + KHS.$$

The liquid turns red, and after a few seconds deposits a white crystalline precipitate of sulphisatyde, which must be washed with boiling alcohol and dried. It generally has a faint rose tint, due to the presence of a small quantity of iodine.

Sulphisatyde when pure is a white, crystalline, inodorous, and tasteless powder; it crystallises from hot alcohol in microscopic rectangular scales. It is insoluble in *water*. Boiling *alcohol* dissolves only traces, which separate out on cooling in small crystalline scales. It is not more soluble in *ether* than in alcohol.

Sulphisatyde, when *heated*, melts, turns red, swells up, and decomposes, while sulphuretted hydrogen is evolved, and a rose-coloured oil distils over, together with the vapour of a substance which crystallises in needles; finally, there remains a bulky residue of charcoal. It is converted by *nitric acid* into a violet powder, which, in all probability, is nitrindin; the solution contains sulphuric acid. It is decomposed by cold *potash* with formation of various products, among which is indin; the solution evolves sulphuretted hydrogen on the addition of hydrochloric acid, and gives a precipitate consisting of sulphur and a little reddish matter. On treating sulphisatyde with warm potash, hydrindin is formed.

Disulphisatyde. $C^{16}H^{12}N^{2}O^{2}S^{2}$. *Sulphésathyde.* (Erdmann, J. p. Chem. xxiv. 16.—Laurent, Ann. Chim. Phys. [3] iii. 463.)—Produced by the action of sulphydric acid upon isatin.

The decomposition takes place in two stages, sulphur being first deposited, and isatyde produced, and this compound being afterwards converted into disulphatyde, with formation of water:

$$\underset{\text{Isatin.}}{2C^{8}H^{5}NO^{2}} + H^{2}S = \underset{\text{Isatyde.}}{C^{16}H^{12}N^{2}O^{4}} + S.$$

and

$$\underset{\text{Isatyde.}}{C^{16}H^{12}N^{2}O^{4}} + 2H^{2}S = \underset{\text{Disulphisatyde.}}{C^{16}H^{12}N^{2}O^{2}S^{2}} + 2H^{2}O.$$

Preparation.—When sulphydric acid gas is passed through a boiling concentrated alcoholic solution of isatin, the liquid becomes pale yellow, and forms a crystalline deposit, which increases on cooling, and consists of microscopic sulphur-crystals and scales (isatyde). The solution is left to itself for a week, that the greater part of the sulphur may crystallise out; it is then poured off and mixed with a little water, and the resulting precipitate is removed, as it contains sulphur; it is then shaken up with more water, which precipitates the disulphisatyde as a brownish grey resinous substance. (Laurent.)

Disulphisatyde, when dried, is a yellowish grey, inodorous, and tasteless powder. It does not crystallise from its alcoholic or ethereal solution, either on cooling or by spontaneous evaporation (Laurent). On drying at 110° it always becomes bluish or brick-red; if the solution is exposed to the air for some time before the addition of water, the precipitate is brownish-red. (Erdmann.)

Disulphisatyde swells up strongly when heated in a glass tube, and melts, with evolution of sulphydric acid; at the same time a brown oil and a needle-shaped sublimate are formed, and there remains a bulky residue of charcoal. When boiled with strong *nitric acid*, it puffs up, evolves pernitric oxide, and dissolves; water precipitates yellow flakes from the solution. In boiling nitric acid diluted with its own bulk of water, it puffs up and gives off nitrous fumes. If the reddish-brown swollen mass is treated, after a few minutes, with alcohol, the latter takes up a reddish substance, which is insoluble in water, but soluble in potash, from which it is precipitated by acids. The portion insoluble in alcohol dissolves in potash, and on neutralising the solution with an acid, a white precipitate, insoluble in water, is formed, consisting of microscopic needles. The liquid obtained by the action of nitric acid contains sulphuric acid, but no oxalic acid. *Bromine* acts violently upon disulphisatyde, with evolution of bromide of sulphur and hydrobromic acid, and forms a yellow mass containing bromindin, an orange-yellow crystalline mass, and a little resin. Disulphisatyde dissolves in strong *sulphuric acid*, with the aid of a gentle heat; the red solution is not precipitated by water; potash colours it green, but does not precipitate it. On treating disulphisatyde with *potash*, sulphisatyde and various other products (amongst others, indin) are formed, which, however, cannot be produced at will. (According to Erdmann, the solution deposits a crystalline salt.) *Ammonia* behaves in a similar manner. With *acid sulphite of ammonium*, at mean temperature, disulphisatyde produces various compounds, among which is found the ammonium-salt of a peculiar acid, called sulphisatanous acid. This salt is crystallisable, soluble in water and alcohol, and its alcoholic solution forms, with dichloride of platinum, a yellow precipitate, which, when decomposed by sulphydric acid, yields the free acid.

When, on the other hand, disulphisatyde is treated with acid sulphite of ammonium at the boiling heat, there is generally deposited a mixture of indin with a white substance which has not been examined; sometimes, however, a different reaction takes place, resulting in the production of *isatan* (p. 404).

ISERIN. Titaniferous iron. See TITANATES.

ISETHIONIC ACID. $C^2H^6SO^4 = C^2H^4.SO^4H^2$. (Gm. viii. 428.—Gerh. ii. 234.) —This acid, which is isomeric with ethyl-sulphuric (sulphovinic) acid, and may be regarded as ethylene-sulphurous acid, $\left.\begin{matrix}(C^2H^4)''\\(SO)''\\H^2\end{matrix}\right\}O^3$, was discovered by Magnus in 1833 (Pogg. Ann. xxvii. 378), and has been further examined by Liebig, Regnault, Woskresensky, Berzelius, Kolbe (Ann. Ch. Pharm. cxii. 241), and Carius (*ibid.* cxxiv. 257). It is produced:—1. By the ebullition of ethionic acid (ii. 523).—2. By the prolonged action of strong sulphuric acid, or of sulphuric anhydride, on alcohol or ether, and is found among the residues of the preparation of ether.—3. By the action of nitrous acid upon taurine, $C^2H^7NSO^3$, which may be regarded as the amic acid of isethionic acid. A solution of taurine in dilute nitric acid, treated with nitrite of potassium, is converted into isethionate of potassium. (W. Gibbs, Sill. Am. J. [2] xxv. 30.)

Preparation.—1. Vapour of sulphuric anhydride is passed into absolute alcohol cooled by a mixture of ice and salt; and the resulting yellowish oily liquid is mixed with water, boiled for some time, and then saturated with carbonate of barium. The product thus obtained is isethionate of barium; if the water were added gradually, and the liquid were not boiled, ethionate of barium would be produced, but no isethionate.—2. Vapour of sulphuric anhydride is passed for some time into anhydrous ether; water is then added, which separates the excess of ether containing heavy oil of wine; and the solution is heated to ebullition; it then gives off, first ether, then alcohol, and ultimately contains nothing but sulphuric and isethionic acids, which may be separated by saturation with carbonate of barium.

To obtain the free acid, the barium-salt is cautiously decomposed with the exact quantity of sulphuric acid required, and the filtrate is evaporated, first by gentle heating, then in a vacuum over oil of vitriol.

Isethionic acid is a viscid, strongly acid liquid, which decomposes acetates and common salt. It bears without decomposition a heat of 150°, but blackens at higher temperatures.

The *isethionates*, $C^2H^5MSO^4$, are obtained by decomposing the barium-salt with solutions of the corresponding sulphates. They are soluble and crystallisable, and are distinguished from the ethyl-sulphates, with which they are isomeric, by their much greater stability, most of them sustaining, without alteration, a temperature of 200°. When an isethionate is heated with caustic potash, hydrogen is evolved, and there remains a mixture of carbonate, oxalate, sulphate, and sulphite, the proportion of these products varying with the degree of heat which has been applied. Isethionate of potassium, distilled with pentachloride of phosphorus, yields $C^2H^4SO^2Cl^2$, or $\begin{matrix}(C^2H^4)''\\(SO)''\end{matrix}\left\{\begin{matrix}O\\Cl^2\end{matrix}\right.$, which, when heated in sealed tubes with ammonia, yields taurine (Kolbe):

$$C^2H^4SO^2Cl^2 + NH^3 + H^2O = C^2H^7NSO^3 + 2HCl.$$

Isethionate of ammonium, $C^2H^5(NH^4)SO^4$, forms well-defined octahedrons, which preserve their transparency in a vacuum, and do not lose weight at 120°.

The *barium-salt*, $C^2H^5BaSO^4$, crystallises in transparent six-sided plates, which may be heated to 300° without loss of weight. They melt at 320°, and decompose at a stronger heat, the salt blackening, swelling up to more than 100 times its original volume, and giving off a liquid of very pungent odour.

The *copper-salt*, $C^2H^5CuSO^4 . H^2O$, forms pale-green right prisms with rhombic base, and bevelled with two faces resting upon the acute edges. At 140° it turns white, and gives off 19·7 per cent. water of crystallisation.

The *potassium-salt*, $C^2H^5KSO^4$, forms rhomboidal prisms which are unalterable in the air, and bear without decomposition a heat of 300°. It melts between 300° and 350°, forming a liquid which, on cooling, solidifies into a fibrous mass having the appearance of porcelain, and undiminished in weight. The salt crystallises readily from boiling alcohol.

ISOBIURET. $C^2H^5N^3O^2$.—A compound isomeric with biuret (i. 600), produced by the action of ammonia on tribrom-acetyl-carbamide:

$$\underset{\text{Tribrom-acetyl-carbamide.}}{CH^3(C^2Br^3O)N^2O} + NH^3 = \underset{\text{Isobiuret.}}{C^2H^5N^3O^2} + \underset{\text{Bromoform.}}{CHBr^3}$$

It dissolves sparingly in cold, easily in hot water, and crystallises from the solution in long needles containing $C^2H^5N^3O^2.2H^2O$, and melting at 185°, whereas biuret forms indistinct crystalline aggregations, and melts at 177°. In all other respects, the two substances resemble each other exactly. (A. Baeyer, Ann. Ch. Pharm. cxxx. 154.)

ISOBROMOMALEIC ACID. See Maleic acid.

ISOCAJPUTENE. See Cajputene (i. 311).

ISOCETAMIDE. See the next article.

ISOCETIC ACID. $C^{15}H^{30}O^2$.—An acid discovered in 1854 by Bouis (Compt. rend. xxxix. 923). It is produced by saponifying the oil of *Jatropha Curcas* (huile de médicinier), the quantity obtained being 18 or 20 per cent. of the weight of the oil. After separation by pressure from oleic acid, and crystallisation from alcohol, it forms shining scales which melt at 55°, and solidify again at 53·5°. Its *silver-salt* is soluble in water, very soluble in alcohol, melts when heated, and burns easily without odour, leaving a residue of metallic silver.

Isocetate of Ethyl, $C^{15}H^{29}(C^2H^5)O^2$, prepared by the usual methods, is odourless, melts at the heat of the hand, and solidifies at 21°, remaining perfectly transparent, and assuming a crystalline structure.

Isocetamide, $C^{15}H^{31}NO$, is obtained by heating the oil above mentioned with ammonia in a sealed tube. It is white, nacreous, melts at 67°, and is not attacked by strong potash.

ISOCYANURIC ACID. Syn. with Fulminuric acid.

ISODIBROMOSUCCINIC ACID. See Succinic acid.

ISODIGLYCOL-ETHYLENIC ACID. $C^6H^{10}O^6$. (Barth and Hlasiwetz, Ann. Ch. Pharm. cxxii. 96).—An acid isomeric with diglycol-ethylenic acid (ii. 914), produced by treating milk-sugar with bromine and the product with oxide of silver. A bromine-compound of milk-sugar, $C^6H^{10}O^5Br^2$, (not isolated) appears to be first formed; and this when treated with moist oxide of silver yields bromide of silver, and the acid, $C^6H^{10}O^6$.

The acid is prepared by heating 30 grms. milk-sugar (1 at. = $C^6H^{10}O^5$) with 60 grms. bromine and half a litre of water, to 100° in strong well-closed bottles. The somewhat dilute yellowish solution is neutralised with moist oxide of silver (or oxide of lead); and the filtered solution is decomposed by sulphydric acid, evaporated at a gentle heat, mixed with alcohol to remove a little lime, freed from alcohol by distillation, and saturated, while still hot, with carbonate of cadmium. The slightly acid solution, decolorised with animal charcoal, yields the cadmium-salt in groups of granular crystals. To obtain the free acid, the cadmium-salt is rubbed up to a thin paste with water, and decomposed while hot by sulphydric acid, and the filtrate is evaporated to a syrup, which gradually dries up to a soft, hygroscopic, crystalline mass.—This acid may also be obtained, without the formation of the intermediate bromine-compound, by treating milk-sugar with half the preceding quantity of bromine, neutralising the solution with carbonate of sodium, and boiling.

An acid, agreeing with the preceding in every respect excepting the amount of its rotatory power, is obtained in like manner from gum-arabic. With starch only, a small quantity of an uncrystallisable acid mass is obtained. Mannite, cane-sugar and glucose, treated with bromine and water, form hydrobromic acid, which then gives rise to the formation of humus-like products.

Isodiglycol-ethylenic acid dried over oil of vitriol contains 13·9 per cent. water, agreeing nearly with the formula, $2C^6H^{10}O^6.3H^2O$. It has a strong acid reaction, melts below 100°, and burns on platinum-foil, giving off the odour of burnt sugar. It dissolves in alcohol and is precipitated from the solution in flocks by ether. The aqueous solution is not precipitated by neutral or basic acetate of lead, mercuric nitrate, caustic baryta, or lime-water, but forms a white precipitate with ammoniacal sugar of lead. The ammonium-salt reduces an alkaline cupric solution, and forms a speculum when heated with nitrate of silver. The acid possesses optical rotatory power.

Isodiglycol-ethylenate of ammonium, $C^6H^9(NH^4)O^6.H^2O$, crystallises in large, transparent, glassy crystals of the monoclinic system. It dissolves in water, is nearly insoluble in alcohol, and gives off all its water at 120°.

The *cadmium-salt* crystallises from a hot-saturated solution in granular aggregates of monoclinic needles containing $2C^6H^9CdO^6.3H^2O$; from dilute solutions, or from the mother-liquor by slow evaporation, in well-developed monoclinic crystals, mostly united in tufts. Both these hydrates, especially the former, are sparingly soluble in water, and both retain all their water of crystallisation till heated to 150°.

The *calcium-salt*, $2C^6H^9CaO^6.7H^2O$, crystallises in crusts, or from more dilute solutions in large shining plates; it gives off 4 at. water at 100°, and the rest at 140°. There is also a calcium-salt containing only half as much water as the preceding.

The *barium-* and *strontium-salts* are gummy.

The *copper-salt* is soluble and amorphous.

A *lead-salt* having approximately the composition, $C^6H^9PbO^4.2Pb^2O.\frac{1}{2}H^2O$, is obtained as a white precipitate on treating the solution of the acid with neutral acetate of lead and ammonia.

The *potassium-salt* forms a viscid uncrystallisable mass, easily soluble in water, and precipitated by alcohol.

The *silver-salt* is a gelatinous, easily decomposible precipitate, formed only in concentrated solutions.

The *sodium-salt* forms tufts of prisms, which in the air-dried state contain $C^6H^9NaO^4.2H^2O$, and give off half their water at 100°.

ISOMERISM. This term is derived from *ἴσος* equal, and *μέρος* part, and its employment by chemists is an expression of the fact that very different chemical compounds have sometimes identically the same ultimate composition.

Two or more different bodies which are composed of the same elements, and of the same proportions of those elements (*i.e.* which have the same percentage composition) are said to be isomeric.

Isomerism is sometimes used in a narrower sense, being made to signify equality of molecular weight, as well as identity in percentage composition. When the compounds have the same percentage composition but different molecular weights, the term polymeric is employed. Thus there are the terms *Isomeric* (in its wide sense), signifying that the different bodies have the same percentage composition; *Polymeric*, signifying that these different bodies have the same percentage composition, but different molecular weights; *Isomeric* (in its restricted sense), sometimes called *Metameric*, that the bodies have the same percentage composition and likewise the same molecular weight.

As might naturally be expected, cases of isomerism abound in organic chemistry, where an enormous number of compounds result from the combination of very few elements. The following organic substances may be cited by way of illustrating the employment of the term isomeric and its cogeners.

Butyric acid	$\left.\begin{matrix}C^4H^7O\\H\end{matrix}\right\}O = C^4H^8O^2$
Acetic ether	$\left.\begin{matrix}C^2H^3O\\C^2H^5\end{matrix}\right\}O = C^4H^8O^2$
Aldehyde	$\left.\begin{matrix}C^2H^3\\H\end{matrix}\right\}O = C^2H^4O$
Oxide of ethylene	$(C^2H^4)''O = C^2H^4O$

These four bodies are quite different, and have the same percentage composition, viz.:

Carbon	54·55
Hydrogen	9·09
Oxygen	36·36
	100·00

They are *Isomeric*, or *Isomers*, using the term in its widest sense.

Again, butyric acid and aldehyde have different molecular weights:—

Butyric acid	$C^4H^8O^2$	= 88
Aldehyde	C^2H^4O	= 44

Butyric acid and aldehyde are therefore *Polymeric*.

Similarly acetic ether and aldehyde are *Polymeric*, or acetic ether and oxide of ethylene are *Polymeric*, or butyric acid and oxide of ethylene are *Polymeric*.

Again, butyric acid and acetic ether have the same molecular weights, viz.:

Butyric acid	$C^4H^8O^2$	= 88
Acetic ether	$C^4H^8O^2$	= 88

They are therefore *Isomeric* (in the restricted sense) or *Metameric*. Aldehyde and oxide of ethylene are also metameric bodies.

Closely related to the term isomerism is the term allotropy. Both of them have reference to the same substantial fact, viz. that different substances have sometimes the same ultimate composition; but they differ in their manner of stating it. Isomeric and allotropic are in fact complementary terms, "isomeric" being employed to predicate identity of composition between different bodies, whilst "allotropic" expresses difference between bodies of identical composition.

Such being the force of these words, there is a certain propriety in their usage; thus whilst it is correct to say, "Butyric acid and acetic ether are *isomeric*," it should be "There are *allotropic* bodies of the formula, C^6H^7N." The same reason which enjoins the use of "allotropic" in this case, prescribes it in the instance of single elements; thus, for example, we read of "allotropic kinds of sulphur," but never of isomeric kinds.

It is worthy of remark that cases of isomerism occurring in inorganic chemistry, are usually described by employing the word allotropy or allotropic, whilst the reverse obtains in organic chemistry. This may be partly ascribed to there being always a very wide difference—or else no difference at all—in the composition of any definite inorganic substances; and hence the fact of identity or non-identity of composition being so easily ascertainable, it is implied in the form of expression, whilst the fact of difference of properties alone needs to be made the subject of formal predication. Among organic bodies, on the other hand, it continually happens that the differences of composition are quite decided, and yet so very minute as to tax the utmost powers of chemical analysis for their recognition; and hence the superior dignity which the mere affirmation of identity of ultimate composition acquires in the organic department of the science.

The principal examples of allotropy or isomerism, *i.e.* of the coexistence of identical ultimate composition with difference of properties, will now be considered.

Hydrocarbons.—1. The olefines, a numerous class having the general formula, C^nH^{2n}, form a very remarkable case of polymerism. Methylene, the lowest term, where $n = 1$, is wanting, and appears to be an impossible body; for many reactions in which it should be produced yield the higher terms instead. The olefines at present known are:

		Vapour-density.	Boiling-point.
Ethylene	C^2H^4	0·97	. .
Propylene	C^3H^6	1·45	. .
Butylene	C^4H^8	1·94	. .
Amylene	C^5H^{10}	2·42	35°
Hexylene	C^6H^{12}	2·91	69°
Heptylene	C^7H^{14}	3·39	95°
Octylene	C^8H^{16}	3·87	125°
Decatylene (paramylene)	$C^{10}H^{20}$	4·84	165°
Cetylene	$C^{16}H^{32}$	7·75	275°.

By the destructive distillation of wax, Brodie obtained cerotene, for which the formula $C^{27}H^{54}$ has been given; but there is in reality no reason whatever why $C^{27}H^{54}$, rather than any other out of a considerable number of formulæ, should be assigned to it.

The percentage composition of the olefines is

$$\begin{array}{lr} \text{Carbon} & = \ 85{\cdot}72 \\ \text{Hydrogen} & = \ \underline{14{\cdot}28} \\ & 100{\cdot}00 \end{array}$$

They present a certain general chemical character. All of them combine with chlorine and bromine with great readiness. They differ in vapour-density, those near the beginning of the list increasing regularly in vapour-density by 0·4844. The first two are gaseous at ordinary temperature and pressure; the third is a very volatile liquid boiling at about 0° C.; the others on the list are liquids of which the boiling-point rises as the formula increases; and the very complex olefines which, being uncertain, are not on the list are usually believed to be solids. It will be observed that the increment in boiling point for the addition of CH^2 to the formula is large; between amylene and hexylene, for instance, it is 34°. As the series is ascended, the increment becomes, no doubt, successively smaller and smaller.

The specific gravity of the different olefines in the liquid state seems to increase as the formula increases.

There are certain well ascertained chemical differences between the olefines. Thus the amount of olefine which will saturate a given quantity of chlorine, or of bromine, differs according to the olefine taken, being proportional to the vapour-density. The molecular weights of the different olefines express their saturating capacity: because the vapour-densities are proportional to the molecular weights.

Each olefine may be prepared from a peculiar alcohol, and in general may be made to yield that peculiar alcohol by certain simple processes, *e. g.*:

$$\underset{\text{Ethylic alcohol.}}{C^2H^6O} - H^2O = \underset{\text{Ethylene.}}{C^2H^4}$$

$$\underset{\text{Amylic alcohol.}}{C^5H^{12}O} - H^2O = \underset{\text{Amylene.}}{C^5H^{10}}$$

and again:

$$\underset{\text{Ethylene.}}{C^2H^4} + H^2O = \underset{\text{Ethylic alcohol.}}{C^2H^6O}$$

$$\underset{\text{Amylene.}}{C^5H^{10}} + H^2O = \underset{\text{Amylic alcohol.}}{C^5H^{12}O.}$$

If the alcohol and the olefine standing in these relations to it be compared, it will be seen that they resemble one another in the number of carbon-atoms contained in their molecules.

The explanation that chemists give of the difference between the olefines is that their molecules are of different degrees of complexity, and that, in fact, different carbon-radicles are contained in them. Thus in ethylene we have the carbon radicle, C^2, and accordingly, ethylene is easily obtained from certain compounds containing the radicle C^2, and easily yields derivatives containing the radicle C^2. Again in amylene there is the radicle C^5, and amylene is obtained from compounds of C^5, which it in turn may be made to regenerate.

The olefines present a very curious example of polymerism, being at one and the same time polymeric and homologous. Recent investigations render it probable that there is also isomerism in its restricted sense (or metamerism) among the olefines. It appears that there is more than one body having the formula, C^6H^{12}, the hexylene derived from mannite appearing to be allotropic with that got from other sources (p. 155).

It would seem also that there are distinct varieties of amylene.

(2) Among compounds of the general formula, C^nH^{2n+2}, there is a wide field for metamerism, but polymerism is obviously an impossibility.

Two classes of compounds are commonly recognised as possessing this general formula. These are the alcohol-radicles and the alcohol-hydrides.

Methyl, the simplest alcohol-radicle is metameric with ethyl-hydride.

Methyl . . . . $\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\} = C^2H^6$

Ethyl-hydride . . . . $\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\} = C^2H^6$

And, advancing higher in the series, the possibility of cases of metamerism becomes much greater. Thus putting $n = 6$ in the formula, C^nH^{2n+2}, we have the following metameric compounds, all included by the expressions hydride and alcohol-radicle :

Hexyl-hydride . . . . $\left.\begin{matrix}H\\C^6H^{13}\end{matrix}\right\} = C^6H^{14}$

Methyl-amyl . . . . $\left.\begin{matrix}CH^3\\C^5H^{11}\end{matrix}\right\} = C^6H^{14}$

Ethyl-tetryl . . . . $\left.\begin{matrix}C^2H^5\\C^4H^9\end{matrix}\right\} = C^6H^{14}$

Trityl-trityl . . . . $\left.\begin{matrix}C^3H^7\\C^3H^7\end{matrix}\right\} = C^6H^{14}$

There is, however, no reason for believing that alcohol-radicles and alcohol-hydrides form the only classes of compounds embraced by the formula, C^nH^{2n+2}. Nothing that we know would lead to the rejection of, for instance, the following additional allotropic compounds having the formula, C^6H^{14}.

$$C\left\{\begin{matrix}C^2H^5\\C^2H^5\\CH^3\\H\end{matrix}\right.;\quad C\left\{\begin{matrix}C^2H^5\\CH^3\\CH^3\\CH^3\end{matrix}\right.;\quad C\left\{\begin{matrix}C^3H^7\\C^2H^5\\H\\H\end{matrix}\right.;\quad C\left\{\begin{matrix}C^3H^7\\CH^3\\CH^3\\H\end{matrix}\right.;\quad C\left\{\begin{matrix}C^4H^9\\CH^3\\H\\H\end{matrix}\right.;\quad C\left\{\begin{matrix}C^5H^{11}\\H\\H\\H\end{matrix}\right.$$

Respecting the actual differences between isomers having the general formula C^nH^{2n+2}, very little is positively known. A difference in the action of dry chlorine upon methyl and hydride of ethyl, has been observed by Frankland, methyl yielding $C^2H^4Cl^2$ as a gaseous compound, whereas ethyl-hydride gives $C^2H^4Cl^2$ as a liquid.

Schorlemmer, on the other hand, who has experimented under different conditions, obtains from methyl a body which has the composition, vapour-density, and boiling point of chloride of ethyl. He has not, however, obtained common alcohol from it, and whether it be or be not identical with chloride of ethyl remains, for the present, undecided.

The hydride of tetryl, which occurs in petroleum, is a very volatile liquid, boiling at about 0° ; ethyl is a gas which does not condense at $-18°$, under the ordinary atmospheric pressure.

Hydride of tetryl and ethyl are metameric. $\left.\begin{matrix}C^4H^9\\H\end{matrix}\right\} = \left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.$.

The hexyl-hydride derived from mannite by the action, first of hydriodic acid, and then of zinc and alcohol, is remarkably insensible to the action of chlorine, even in the presence of iodine and water. The hydride of hexyl occurring in petroleum, on the other hand, seems to be readily attacked by that agent.

The circumstance that those β hexyl compounds from which the hexyl-hydride of mannite is more immediately derived, tend to split up on oxidation, lends some kind of support to the notion that the formula for the mannite-hydride is

$$C\left\{\begin{matrix}C^2H^5\\CH^3\\CH^3\\CH^3\end{matrix}\right.$$

but much remains to be done before any very positive opinion can be formed of the nature of the metamerism subsisting between this mannite-hydride and the commoner hexyl-hydride.

3. Two compounds with the empirical formula CH, viz. benzene and acetylene, present a curious case of polymerism.

These compounds have a certain likeness, both being products of the action of a very elevated temperature, but in other respects they are very unlike.

Benzene, $C^{6}H^{6}$, is a liquid, and is related to benzoic acid and phenylamine. Acetylene, $C^{2}H^{2}$, is a gas possessing the peculiar property of attacking certain metallic solutions, such as ammoniacal solution of cuprous chloride, and is related to common alcohol.

4. A large number of volatile oils differing much in smell, taste, boiling-point, action with reagents, and in other important particulars, have had the formula $C^{10}H^{16}$ assigned to them. To this class belong the different kinds of oil of turpentine, oil of lemons, neutral oil of cloves, oil of elemi-resin, carvene, and some others. Respecting these bodies, the remark may be made that we are, for the most part, quite ignorant of their true formula: for, in the almost entire absence of derivatives, the mere analysis of such hydrocarbons by our present methods is totally inadequate to distinguish between a variety of non-isomeric formulæ, all equally probable.

Isomers containing Carbon, Hydrogen, and Oxygen.

Both metamerism and polymerism occur very abundantly among these compounds.

(1.) The ethers of the organic acids afford room for endless metamerism, as will be apparent on a little consideration.

Acetate of methyl, $\left.\begin{matrix}C^{2}H^{3}O\\CH^{3}\end{matrix}\right\}O$, is metameric with formate of ethyl, $\left.\begin{matrix}CHO\\C^{2}H^{5}\end{matrix}\right\}O$, and with propionic acid, $\left.\begin{matrix}C^{3}H^{5}O\\H\end{matrix}\right\}O$. It is obvious that if we subtract nCH^{2} from the acid-forming radicle and add nCH^{2} to the alcohol-forming radicle, or *vice versâ*, we must get a metamer. Hence it follows that any ether of an organic acid must have many metamers, if its molecular weight be tolerably high. Here is an example:—

Valerate of amyl . . .	$\left.\begin{matrix}C^{5}H^{9}O\\C^{5}H^{11}\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$
Butyrate of hexyl . . .	$\left.\begin{matrix}C^{4}H^{7}O\\C^{6}H^{13}\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$
Propionate of heptyl . . .	$\left.\begin{matrix}C^{3}H^{5}O\\C^{7}H^{15}\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$
Acetate of octyl	$\left.\begin{matrix}C^{2}H^{3}O\\C^{8}H^{17}\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$
Formate of nonyl . . .	$\left.\begin{matrix}CHO\\C^{9}H^{19}\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$
Caproate of tetryl . . .	$\left.\begin{matrix}C^{6}H^{11}O\\C^{4}H^{9}\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$
Œnanthate of trityl . . .	$\left.\begin{matrix}C^{7}H^{13}O\\C^{3}H^{7}\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$
Caprylate of ethyl . . .	$\left.\begin{matrix}C^{8}H^{15}O\\C^{2}H^{5}\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$
Pelargonate of methyl . .	$\left.\begin{matrix}C^{9}H^{17}O\\CH^{3}\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$
Rutic acid	$\left.\begin{matrix}C^{10}H^{19}O\\H\end{matrix}\right\}O$	=	$C^{10}H^{20}O^{2}$

Thus there are no fewer than nine metamers of valerate of amyl. The difference between metamers of this kind is very neatly defined by reactions, saponification with potash yielding a different alcohol and a potassium-salt of a different acid in each case. For example, valerate of amyl gives amyl-alcohol and valerate of potassium, whilst butyrate of hexyl gives hexyl-alcohol and butyrate of potassium.

This kind of metamerism is, of course, not confined to the fatty-acid series: whenever there are homologues of the acids—no matter what the series to which the acid belongs—such metamerism is possible. And of course the same remark applies to the alcohol, the aromatic and the allylic series admitting of just the same kind of metamerism as the vinic series.

(2.) Every alcohol in a series, except the lowest one, is metameric with one or more ethers, thus:—

Common alcohol	$\left.\begin{matrix}C^{2}H^{5}\\H\end{matrix}\right\}O$	=	$C^{2}H^{6}O$

Methyl-ether . . . . $\left.\begin{matrix}CH^3\\CH^3\end{matrix}\right\}O$ = C^2H^6O.

or higher up in the scale:—

Amyl-alcohol . . . . $\left.\begin{matrix}C^5H^{11}\\H\end{matrix}\right\}O$ = $C^5H^{12}O$

Tetryl-methyl ether . . . . . . $\left.\begin{matrix}C^4H^9\\CH^3\end{matrix}\right\}O$ = $C^5H^{12}O$

Trityl-ethyl ether . . . . . . $\left.\begin{matrix}C^3H^7\\C^2H^5\end{matrix}\right\}O$ = $C^5H^{12}O$.

The action of iodide of phosphorus upon these different compounds enables us to distinguish them immediately.

(3.) The aldehydes are metameric with ketones, with alcohols of the allylic series, and with ethers of the glycol series, thus:

Propylic aldehyde . . . . . . $\left.\begin{matrix}C^3H^5O\\H\end{matrix}\right\}$ = C^3H^6O

Common acetone . . . . . . $\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}$ = $C^3H\ O$

Allylic alcohol . . . . $\left.\begin{matrix}C^3H^5\\H\end{matrix}\right\}O$ = C^3H^6O

Oxide of tritylene . . . . . . $(C^3H^6)''O$ = C^3H^6O.

These four compounds are very easily distinguished from one another: the first is easily oxidised to propionic acid; the second gives no propionic acid on oxidation, but lower fatty acids instead; the third gives acrolein and acrylic acid; the fourth lactic acid.

(4.) Ketones are metameric with other ketones and with aldehydes and compounds metameric therewith.

The metamerism with other ketones is very easy to understand. The rational formula of all ketones consisting of an acid-forming radicle conjoined with an alcohol-forming radicle, it follows that transference of nCH^2, from one radicle to the other will yield isomeric bodies. Thus, for instance, we have isomers in

Methyl-valeryl . . $\left.\begin{matrix}C^5H^9O\\CH^3\end{matrix}\right\}$ and Ethyl-butyryl . . $\left.\begin{matrix}C^4H^7O\\C^2H^5\end{matrix}\right\}$

Our knowledge of the ketones is very slight, but it is to be expected that these two compounds would give different products on being oxidised.

Metameric Alcohols.—It has recently been discovered that there are at least two series of alcohols, the corresponding terms of which are metameric, well-marked differences having been recognised between compounds with the composition of hexylic alcohol, and also between compounds with the composition of amylic alcohol. It is at present uncertain what the nature of this metamerism is (see HEXYL-ALCOHOLS, p. 152), but it seems to affect the total constitution of the two sets of compounds.

A more superficial kind of difference was noticed by Pasteur, some years ago, between varieties of amylic alcohol. Ordinary fusel-oil was found by Pasteur to be made up of two liquids having the composition of amylic alcohol, but slightly different in properties, the one being without action on polarised light, whilst the other turned the plane of a polarised ray to the left. The derivatives of each of these varieties of amylic alcohol possess the same action on polarised light as the alcohols themselves, and present some differences in solubility, &c., but on the whole they are marvellously similar. Chemists are not agreed how these varieties are to be regarded, it being still uncertain whether a mere difference in action upon polarised light points to any but the very slightest difference in constitution.

Metameric Acids.—There is some reason for believing that the fatty acids, when they are in the liquid state, have twice the molecular weight which their vapours have when heated up to 300° and higher. Their great tendency to form double salts, and the fact that their vapours at low temperature—whether under great or small pressure—have a double density, point to this conclusion.

Admitting the double formula for the fatty acids, some very interesting cases of metamerism arise. Thus, propionic acid is metameric with butyr-acetic acid:—

Propionic acid . . . $\left.\begin{matrix}C^3H^5O\\C^3H^5O\\H^2\end{matrix}\right\}O^2 = C^6H^{12}O^4$,

Butyr-acetic acid . . . $\left.\begin{matrix}C^4H^7O\\C^2H^3O\\H^2\end{matrix}\right\}O^2 = C^6H^{12}O^4$, and, in like manner, each term of the series, except the end ones, is metameric with a compound acid formed of the next below united with the next above. It is worthy of remark, as a fact in the history of organic chemistry, that butyr-acetic acid was mistaken for, and described as, propionic acid.

The anhydrides of the aromatic and fatty acids offer a systematic metamerism, *e.g.*:

$$\text{Aceto-valeryl anhydride} \quad . \quad . \quad \left.\begin{matrix} C^2H^3O \\ C^5H^9O \end{matrix}\right\} O = C^7H^{12}O^3,$$

and

$$\text{Propio-butyryl anhydride} \quad . \quad \left.\begin{matrix} C^3H^5O \\ C^4H^7O \end{matrix}\right\} O = C^7H^{12}O^3,$$

are metameric. In fact there is, among these anhydrides, just a repetition of the case of the ethereal-salts of the organic acids; by making nCH^2 move from the one radicle to the other, endless metamerism arises.

No case of metamerism between two single fatty acids has yet been made out; but in the aromatic series, there are such cases: thus there are two benzoic acids.

A very remarkable example of metamerism is afforded by the different varieties of tartaric acid and racemic acid. There is a tartaric acid which polarises to the right (the commonest), another which polarises to the left; racemic acid, from which both varieties of tartaric acid may be obtained; and, finally, a tartaric acid without any action upon polarised light. All these substances are metameric, having the formula

$$C^4H^6O^6.$$

Polyatomic Alcohols.—Mannite and melampyrin are metameric, both of them having the formula

$$C^6H^{14}O^6.$$

The most striking difference between these bodies is to be found in their degrees of solubility in water—mannite being comparatively soluble, melampyrin comparatively insoluble. In reactions they are, so far as is known, very similar.

There seem to be many metamers both of grape-sugar and of cane-sugar, but little is known with certainty respecting them.

Examples of polymerism are not by any means so numerous among the compounds of carbon, hydrogen, and oxygen, as we have found the examples of metamerism to be.

There can be no polymers either of the vinic alcohols or vinic ethers.

The fatty acids, and the ethers of the fatty acids, are polymeric with more complex acids, or with compounds of the sugar-class; but even among them, there is nothing approaching to the endless metamerism which has been referred to.

Acetic acid offers one of the best examples of a fatty acid polymeric with several substances:

$$2(CH^2O) = C^2H^4O^2, \text{ acetic acid,}$$
$$3(CH^2O) = C^3H^6O^3, \text{ lactic acid,}$$
$$6(CH^2O) = C^6H^{12}O^6, \text{ grape-sugar.}$$

By doubling the formula of any aldehyde, we get the formula of a fatty acid, thus:

$$C^2H^4O, \text{ common aldehyde,}$$
$$C^4H^8O^2, \text{ butyric acid.}$$

By tripling the formula of an aldehyde, we get the formula of an acid of the lactic series, *e.g.*:

$$C^2H^4O, \text{ common aldehyde,}$$
$$C^6H^{12}O^3, \text{ leucic acid.}$$

Grape-sugar is polymeric with ethyl-carbonic acid: Grape-sugar = $C^6H^{12}O^6$; 2 molecules of ethyl-carbonic acid = $2.\left.\begin{matrix} CO \\ C^2H^5 \\ H \end{matrix}\right\} O^2 = 2C^3H^6O^3 = C^6H^{12}O^6$.

Isomers containing Carbon, Hydrogen, and Nitrogen.

(1.) *Metamerism among the compound ammonias.*

The following compound ammonias have the formula $C^6H^{15}N$:—

$$\text{Hexylamine} \quad . \quad . \quad . \quad . \quad \left.\begin{matrix} C^6H^{13} \\ H \\ H \end{matrix}\right\} N = C^6H^{15}N$$

$$\text{Amyl-methylamine} \quad . \quad . \quad \left.\begin{matrix} C^5H^{11} \\ CH^3 \\ H \end{matrix}\right\} N = C^6H^{15}N$$

$$\text{Tetryl-ethylamine} \quad . \quad . \quad . \quad \left.\begin{matrix} C^4H^9 \\ C^2H^5 \\ H \end{matrix}\right\} N = C^6H^{15}N$$

$$\text{Tetryl-dimethylamine} \quad . \quad . \quad \left.\begin{array}{r} C^4H^9 \\ CH^3 \\ CH^3 \end{array}\right\} N = C^6H^{15}N$$

$$\text{Di-tritylamine} \quad . \quad . \quad . \quad \left.\begin{array}{r} C^3H^7 \\ C^3H^7 \\ H \end{array}\right\} N = C^6H^{15}N$$

$$\text{Trityl-ethyl-methylamine} \quad . \quad \left.\begin{array}{r} C^3H^7 \\ C^2H^5 \\ CH^3 \end{array}\right\} N = C^6H^{15}N$$

$$\text{Tri-ethylamine} \quad . \quad . \quad . \quad \left.\begin{array}{r} C^2H^5 \\ C^2H^5 \\ C^2H^5 \end{array}\right\} N = C^6H^{15}N.$$

A very neat reaction distinguishes the different compound ammonias from one another: on treating them with nitrous acid, they give up their different alcohol-radicles in the form of alcohols. For example, the first base on our list, hexylamine, when so treated, would yield hexyl-alcohol; the second, amyl-alcohol and methyl-alcohol; the third, tetryl-alcohol and ethyl-alcohol, &c.

According to the foregoing, triethylamine has six distinct metamers: but if, as is by no means unlikely, each one of the three atoms of hydrogen in ammonia has a different function, then the metamers of triethylamine will become very numerous indeed.

It will be obvious that the higher we go—the higher the molecular weight of a base—the more numerous are the possible metamers. Thus tricetylamine, $\left.\begin{array}{r} C^{16}H^{33} \\ C^{16}H^{33} \\ C^{16}H^{33} \end{array}\right\} N$, has upwards of 300 metamers, each of which should give a different result with nitrous acid.

In addition to this kind of metamerism, due to the presence of different alcohol-radicles in the bases, there are other kinds of metamerism among the compound ammonias.

There is, for instance, the well-known case of the bases parallel with phenylamine, benzylamine, &c.

Phenylamine = C^6H^7N = Picoline
Benzylamine = C^7H^9N = Lutidine.
&c. &c. &c.

The probable explanation of the metamerism in this case is that phenylamine is a derivative of benzene, (C^6H^6), whilst picoline is derived from a hydrocarbon C^6H^{10}.

Phenylamine = $(C^6H^5)NH^2$
Picoline = $(C^6H^7)'''N$.

But, whatever may be the nature of the difference in constitution between these two bases, the difference in properties is very striking:

Phenylamine boils at 185°:	Picoline boils at 135°:
very slight smell:	most pungent and bad smell:
almost insoluble in water:	very soluble in water:
specific gravity at 0° = 1·0361;	specific gravity at 0° = 0·9613.
gives rosaniline or mauveine, &c. on treatment with various oxidising agents.	

and the contrast might be carried much further.

A third series of bases, metameric with the foregoing has been discovered. The best investigated term of this series is β-lutidine, which is obtained by the destructive distillation of cinchonine. It is less soluble in water than common lutidine, boils rather higher, has a different smell, &c.

It is possible for two atoms of nitrogen to coalesce and form a group requiring either two or four hydrogen representatives for its saturation. Three or even four atoms of nitrogen also coalesce. Among the bases so resulting there must be almost infinite metamerism.

(2.) *Polymerism among the Compounds of Carbon, Hydrogen, and Nitrogen.*

Cyanide of ethyl and cyanethine are polymeric, the formula of the latter being three times that of the former.

C^3H^5N = Cyanide of ethyl.
$C^9H^{15}N^3$ = Cyanethine.

The former is a liquid, the latter a solid possessing the properties of a weak base. It is probable that the rational formula of the latter is:

$$N^3\left\{\begin{array}{l}C^2H^{3'''}\\C^2H^{3'''}\\C^2H^{3'''}\end{array}\right.$$

It will be obvious that the existence of compound ammonias containing more than one atom of nitrogen in the molecule opens the door for much polymerism.

Isomers containing Carbon, Hydrogen, Nitrogen, and Oxygen.

The metamerism between cyanate of ammonium and urea, is one of the oldest known:

Cyanate of ammonium . . . . . . $\left.\begin{array}{r}CN\\NH^4\end{array}\right\}O = CH^4N^2O$

Urea . . . . $\left.\begin{array}{r}CO''\\H^4\end{array}\right\}N^2 = CH^4N^2O.$

Although cyanate of ammonium is transformed spontaneously into urea, yet there is a very great difference between the characters of the two compounds. One striking difference between a solution of a cyanate and a solution of urea is the comparative stability of the latter.

Glycocine and nitrite of ethyl are metameric:

Glycocine . . . . $\left.\begin{array}{r}C^2H^2NH^2O\\H\end{array}\right\}O = C^2H^5NO^2,$

Nitrite of Ethyl . . . . $\left.\begin{array}{r}NO^2\\C^2H^5\end{array}\right\} = C^2H^5NO^2,$

but are utterly different in properties. Glycocine (sugar of gelatin) is a crystalline solid. Nitrite of ethyl is a liquid.

Anthranilic acid	$C^7H^7NO^2$
Benzamic acid	$C^7H^5NH^2O^2$
Salicylamide	$C^7H^5NH^2OO$
Nitrotoluene	$C^7H^7NO^2$

are metameric.

Besides these, there are many more examples of metamerism among compounds of carbon, hydrogen, nitrogen, and oxygen, but we need not particularise them.

Polymerism also occurs in abundance. A very frequently cited example of this is afforded by

Cyanic acid	$CHNO$
Cyanuric acid	$C^3H^3N^3O^3$

Fulminic acid, $C^2H^2N^2O^2$, is also polymeric with the above, but it is only known in the form of its salts—not in the free state.

Organic Isomers containing various elements in addition to the so-called Organic Elements.

They are very abundant. A good example of metamerism between chlorinated compounds is afforded by dichloride of ethylene and chloride of monochlorethyl:

Dichloride of ethylene, $(C^2H^4)''Cl^2$,	Chloride of monochlorethyl, C^2H^4ClCl;
boils at 85°;	boils at 64°;
specific gravity at 18° = 1·247;	specific gravity at 17° = 1·174;
with alcoholic solution of potash, gives $C^2H^3Cl + HCl$;	with alcoholic solution of potash, hardly any reaction;
with sodium in presence of ether gives $C^2H^4 + 2NaCl$;	with potassium gives no reaction.

A very interesting case, from the extreme simplicity of the compounds, is to be found between the chlorine-derivative obtained by direct action of chlorine on marsh gas, and common chloride of methyl. Both of these compounds have the empirical molecular formula, CH^3Cl, and both are gaseous at ordinary temperatures and pressures, but they possess some unmistakable differences in properties.

There are corresponding brominated compounds—Bunsen obtained a gas from bromhydrate of cacodylic acid. The composition of the gas is the same as that of bromide of methyl, viz., CH^3Br; but whilst bromide of methyl is a liquid boiling at 13°, Bunsen's brominated gas does not liquefy below −17° C.

Many more cases of isomerism among these semi-organic and semi-inorganic compounds might be cited.

Isomers among Inorganic Substances.

As before remarked, the instances of inorganic isomerism are usually called instances of allotropy—isomeric substances and allotropic substances being nearly equivalent expressions.

The elementary substances themselves offer many examples of isomerism. Thus oxygen appears to be capable of existing in two allotropic states; in one condition it is known as ordinary oxygen, in the other as ozone. Ozone and oxygen are isomeric bodies. Formula for oxygen = O^2; formula for ozone = O^4 (?) Experiment has shown that the molecular formula for ozone is higher than that for oxygen; but how much higher remains an open question.

Sulphur, phosphorus, carbon, and many other elements present *somewhat* similar examples of allotropy or isomerism.

Inorganic compounds, such as the various forms of silicic acid, of sesquioxide of iron, of sesquioxide of chromium, of alumina, must be classed among substances affording examples of isomerism.

There seem to be two allotropic states of peroxide of nitrogen. The compound NO^2 is a deeply-coloured gas at 100°. The compound N^2O^4 is a liquid boiling a little below 30°. Its vapour-density is double that of the former body. Altogether, inorganic isomerism is a very wide, but as yet a very ill-explored field.

The explanation of the existence of isomerism will have become sufficiently clear from the course which has been followed in describing the different examples of it. "It is of consequence how the atoms of a compound are arranged as well as what kind of atoms they are," and hence there may be very many totally different substances composed of the same ultimate atoms. This is in fact the whole philosophy of isomerism.

J. A. W.

ISOMORPHISM. (*ἴσος*, equal, and *μορφή*, form.) Crystalline form affords, as is well known, one of the most valuable physical distinctions between different substances, inasmuch as each element, and each compound, crystallises for the most part in forms which are reducible to one or two primary forms. Hauy, who first directed attention to the importance of this character, laid it down as a general law, that every substance has a primary crystalline form peculiar to itself, and therefore that a difference in the primary forms of two crystals may always be taken as evidence of difference of composition. But towards the end of the last, and the beginning of the present century, various observations were made tending to disprove the generality of this law. The similarity of form between phosphate of calcium (apatite) and phosphate of lead (pyromorphite) was noticed by Werner. Leblanc in 1787, showed that a mixed solution of ferrous and cupric sulphates deposits crystals containing both copper and iron, always of the same form, but with considerable variations in the proportions of the two metals; also that alum containing a considerable quantity of ferric oxide crystallises exactly in the same form as pure alumino-potassic sulphate. Vauquelin, in 1797, showed that the same form is exhibited by alum, when it contains a considerable quantity of ammonia in place of potash. Berthier, in 1806, pointed out the great similarity in the form of calc-spar, bitter spar, and spathic iron—a resemblance confirmed by the more exact measurements of Wollaston; and Gay-Lussac, in 1816, showed that a crystal of potash-alum immersed in a solution of ammonia-alum increases in bulk without alteration of form. These and other isolated observations of similar import may be said to have prepared the way for the establishment, by Mitscherlich, of the general law of isomorphism, which affirms that *bodies having a similar chemical constitution have also the same crystalline form, as determined by the measurement of their angles*, or, in other words, that *analogous elements and groups of elements may replace one another in composition without essential alteration of crystalline form.* Mitscherlich's first observations, presented to the Berlin Academy of Sciences in 1819, related to the isomorphism of the phosphates and arsenates, and showed that the corresponding salts of phosphoric and arsenic acids containing equal numbers of atoms of water, crystallise in the same forms. Similar observations were subsequently made upon the sulphates, selenates, manganates, and chromates; the protosalts of magnesium, zinc, cadmium, manganese, iron, nickel, cobalt, and copper, and the sesquisalts of iron, aluminium, chromium, and manganese, the corresponding salts being supposed in all cases to contain equal numbers of atoms of water.

Bodies having apparently an exactly similar constitution are not necessarily isomorphous, but are rather divisible into two or more groups, of which the respective members are isomorphous; on the other hand, the possession of an equal number of atoms is not essential to isomorphism, for two atoms of one element are not unfrequently isomorphous with one atom of another element; and sometimes a molecular group is isomorphous in its combinations with an elementary atom—NH^4 with K, for example. There are also numerous examples of bodies crystallising in the same forms, but without exhibiting any similarity of chemical constitution.

The corresponding angles of isomorphous bodies are not always precisely equal, but may differ from each other by one or two degrees. This discrepancy, however, is rendered unimportant by the circumstance, that the angles of different crystals of one and the same substance can present similar variations, under the influence of certain modifying causes.

It will of course be understood that the similarity of form in isomorphous bodies relates to the primary forms to which they are reducible; two crystals may be really isomorphous, and yet very different in external form, in consequence of being differently modified; thus calc-spar, bitter spar, and spathic iron have the same primary form; but each exhibits numerous modifications, some of which prevail chiefly in one, some in another, of these compounds.

The following table exhibits the most important and best established examples of isomorphism, arranged according to the crystallographic systems. Bodies crystallising in the same forms (*i. e.* reducible to the same primary form) are arranged in groups, numbered consecutively, without regard to the system to which the several forms belong; the subdivisions *a*, *b*, *c*, &c., include those also which correspond in atomic constitution.[*]

TABLE I.

Monometric or *Regular System.*

Group 1. (Holohedral forms.)

a. Diamond,—Phosphorus,—Potassium,—Sodium,—Titanium,—Cadmium,—Lead,—Copper,—Silver,—Gold,—Platinum,—Palladium,—Iridium,—Tin (Frankenheim),—Zinc (Nicklès).

b. ZznS,—MmnS,—PpbS,—PpbSe,—$\mathrm{Ag^2S}$,—$\mathrm{NniS.2FfeS}$ (Scheerer),—MmgO (periclase, according to Scacchi),—NniO (formed in a metallurgic process),—PpbO,—CcuO (tetrahedral),—UuO.

c. KCl,—NaCl,—LiCl,—$\mathrm{NH^4Cl}$,—AgCl,—CcuCl,—KI,—NaI,—KBr,—NaBr,—KF,—NaF,—$\mathrm{KCy.NaCy}$,—$\mathrm{NH^4Cy}$ (Gay-Lussac).

c′. $\mathrm{ZznI^2}$,—$\mathrm{CcaF^2}$,—$\mathrm{KAgCy^2}$,—$\mathrm{NniAS^2}$ (arsenical nickel),—$\mathrm{(Cco;\ Nni)As^2}$ (cobalt-speiss).

d. $\mathrm{CcoAs^3}$ (tesseral pyrites, according to Wöhler and Scheerer).

e. $\mathrm{Ccu^2O}$,—$\mathrm{Ccu^2S}$ (red copper and copper-glance).

f. $\mathrm{As^2O^3}$,—$\mathrm{Sb^2O^3}$,—$\mathrm{Cco^2S^3}$ (cobalt-pyrites).

g. $\left.\begin{matrix}\overset{''}{\mathrm{Mmg}}\\ \overset{'''}{\mathrm{All}}{}^2\end{matrix}\right\}\mathrm{O^4}$ (spinel),—$\left.\begin{matrix}(\mathrm{Mmg};\ \mathrm{Ffe})''\\ {}'''\mathrm{All}^2\end{matrix}\right\}\mathrm{O^4}$ (pleonast),—$\left.\begin{matrix}\overset{''}{\mathrm{Mmg}}\\ \overset{'''}{\mathrm{Ffe}}{}^2\end{matrix}\right\}\mathrm{O^4}$ (chlorospinel),—$\left.\begin{matrix}\overset{''}{\mathrm{Zzn}}\\ \overset{'''}{\mathrm{All}}{}^2\end{matrix}\right\}\mathrm{O^4}$ (gahnite),—$\left.\begin{matrix}\overset{''}{\mathrm{Zzn}}\\ \overset{'''}{\mathrm{Ffe}}{}^2\end{matrix}\right\}\mathrm{O^4}$ (franklinite),—$\left.\begin{matrix}\overset{''}{\mathrm{Ffe}}\\ \overset{'''}{\mathrm{Ffe}}{}^2\end{matrix}\right\}\mathrm{O^4}$ (magnetic iron ore),—$\left.\begin{matrix}\overset{''}{\mathrm{Ffe}}\\ \overset{'''}{\mathrm{Ccr}}{}^2\end{matrix}\right\}\mathrm{O^4}$ (chrome iron ore, according to Abich).

h. $\mathrm{BbaN^2O^6}$,—$\mathrm{SsrN^2O^6}$,—$\mathrm{PpbN^2O^6}$. (Berzelius.)

i. $\mathrm{K^2}\overset{''''}{\mathrm{Ppt}}\mathrm{Cl^6}$,—$\mathrm{K^2}\overset{''''}{\mathrm{Irr}}\mathrm{Cl^6}$,—$\mathrm{K^2}\overset{''''}{\mathrm{Oss}}\mathrm{Cl^6}$,—$\mathrm{(NH^4)^2}\overset{''''}{\mathrm{Ppt}}\mathrm{Cl^6}$,—$\mathrm{(NH^4)^2}\overset{''''}{\mathrm{Irr}}\mathrm{Cl^6}$. (Berzelius.)

k. *Alums*: $\mathrm{(NH^4)}\overset{'''}{\mathrm{All}}\mathrm{(SO^4)^2.12H^2O}$,—$\mathrm{(NH^4)}\overset{'''}{\mathrm{Ccr}}\mathrm{(SO^4)^2.12H^2O}$,—$\mathrm{(NH^4)}\overset{'''}{\mathrm{Mmn}}\mathrm{(SO^4)^2.12H^2O}$,—$\mathrm{(NH^4)}\overset{'''}{\mathrm{Ffe}}\mathrm{(SO^4)^2.12H^2O}$,—$\mathrm{K}\overset{'''}{\mathrm{All}}\mathrm{(SO^4)^2.12H^2O}$,—$\mathrm{K}\overset{'''}{\mathrm{Ccr}}\mathrm{(SO^4)^2.12H^2O}$,—$\mathrm{K}\overset{'''}{\mathrm{Mmn}}\mathrm{(SO^4)^2.12H^2O}$,—$\mathrm{K}\overset{'''}{\mathrm{Ffe}}\mathrm{(SO^4)^2.12H^2O}$,—$\mathrm{Na}\overset{'''}{\mathrm{All}}\mathrm{(SO^4)^2.12H^2O}$ (Mitscherlich),—$\mathrm{Li}\overset{'''}{\mathrm{All}}\mathrm{(SO^4)^2.12H^2O}$ (Kralovansky),—$\mathrm{Ag}\overset{'''}{\mathrm{All}}\mathrm{(SO^4)^2.12H^2O}$ (Church), $\mathrm{Tl}\overset{'''}{\mathrm{All}}\mathrm{(SO^4)^2.12H^2O}$ (Crookes).

l. *Garnets*: $\left.\begin{matrix}\overset{''''}{\mathrm{Si}}{}^3\\ \overset{''}{\mathrm{Cca}}\\ \overset{'''}{\mathrm{All}}{}^2\end{matrix}\right\}\mathrm{O^{12}}$,—$\left.\begin{matrix}\overset{''''}{\mathrm{Si}}{}^3\\ \overset{''}{\mathrm{Mmg}}\\ \overset{'''}{\mathrm{All}}{}^2\end{matrix}\right\}\mathrm{O^{12}}$,—$\left.\begin{matrix}\overset{''''}{\mathrm{Si}}{}^3\\ \overset{''}{\mathrm{Ffe}}\\ \overset{'''}{\mathrm{All}}{}^2\end{matrix}\right\}\mathrm{O^{12}}$,—$\left.\begin{matrix}\overset{''''}{\mathrm{Si}}{}^3\\ \overset{''}{\mathrm{Mmn}}\\ \overset{'''}{\mathrm{All}}{}^2\end{matrix}\right\}\mathrm{O^{12}}$,—$\left.\begin{matrix}\overset{''''}{\mathrm{Si}}{}^3\\ \overset{''}{\mathrm{Cca}}\\ \overset{'''}{\mathrm{Ffe}}{}^2\end{matrix}\right\}\mathrm{O^{12}}$,—

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[*] The larger atomic weights recently assigned to the greater number of the metals (i. 1008, iii. 31) are used in this and the following tables, as in many instances they exhibit the relations between isomorphous compounds more simply than the older atomic weights. Those metals whose atomic weights are here regarded as double of those given in the table of atomic weights (i. 465), are denoted by double symbols, *e.g. barium* Bba, *lead* Ppb, &c.

$$\left.\begin{array}{l}\overset{''''}{\mathrm{Si}}{}^{3}\\ \mathrm{C}\overset{''}{\mathrm{ca}}\\ \overset{'''}{\mathrm{C}}\mathrm{cr}^{2}\end{array}\right\}\mathrm{O}^{16}\ \text{chrome-garnet (according to Komonen).}$$

$$m.\ \left.\begin{array}{l}\overset{''''}{\mathrm{Si}}{}^{2}\\ \mathrm{K}\\ \overset{'''}{\mathrm{A}}\mathrm{ll}\end{array}\right\}\mathrm{O}^{6}\ \text{(leucite).} — n.\ \left.\begin{array}{l}\overset{''''}{\mathrm{Si}}{}^{2}\\ \mathrm{Na}\\ \overset{'''}{\mathrm{A}}\mathrm{ll}\end{array}\right\}\mathrm{O}^{6}.\mathrm{H}^{2}\mathrm{O}\ \text{(analcime).}$$

Group 2. (Hemihedral forms.)

a. $\mathrm{CcoAs^2.CcoS^2}$ (cobalt-glance), — $\mathrm{NniAs^2.NniS^2}$ (nickel-glance), — $\mathrm{NniSb^2.NniS^2}$ (nickel-antimony-glance).
b. $\mathrm{FfeS^2}$ (iron-pyrites).

Dimetric System.

Group 3.

$\mathrm{C}\overset{''}{\mathrm{ca}}\mathrm{Ww^{vi}O^4}$ (tungsten), — $\mathrm{Ppb''.Ww^{vi}O^4}$ (scheeletine), — $\mathrm{Ppb''Mmo^{vi}O^4}$ (wulfenite; Levy), — $\mathrm{Ppb''Ccr^{vi}O^4}$.

Group 4.

$\mathrm{NniSO^4.7H^2O}$, — $\mathrm{NniSeO^4.7H^2O}$, — $\mathrm{ZznSeO^4.7H^2O}$. (Mitscherlich.)

Group 5.

$\mathrm{KH^2PO^4}$, — $\mathrm{KH^2AsO^4}$, — $\mathrm{(NH^4)H^2PO^4}$, — $\mathrm{(NH^4)H^2AsO^4}$. (Mitscherlich.)

Group 6.

$\mathrm{2NH^3.Ag^2SO^4}$, — $\mathrm{2NH^3.Ag^2SeO^4}$, — $\mathrm{2NH^3.Ag^2CrO^4}$. (Mitscherlich.)

Group 7.

$\mathrm{Ccu^3P^2O^8.2\,[(\overset{''}{U}uO)^3P^2O^8]\,24H^2O}$ (copper-uranite), — $\mathrm{Cca^3P^2O^8.2[(U\overset{''}{u}O)^3P^2O^8]\,24H^2O}$ (lime-uranite).

Group 8.

a. $\mathrm{Mmn^2O^3}$ (braunite). (v. Kobell.)
b. $\mathrm{Ccu^2S.Ffe^2S^3}$ (copper pyrites).

Group 9.

$\mathrm{TiO^2}$ (rutile), — $\mathrm{SnO^2}$ (tin-stone).

Hexagonal System.

Group 10.

Arsenic, — Antimony, — Tellurium (Breithaupt), — Osmium, — Iridium, — Palladium, — Bismuth. (G. Rose.)

Group 11.

a. $\mathrm{CcaCO^3}$ (calcspar), — $\mathrm{MmgCO^3}$ (magnesite), — $\left.\begin{array}{l}\frac{1}{2}\mathrm{Mmg}\\ \frac{1}{2}\mathrm{Cca}\end{array}\right\}\mathrm{CO^3}$ (dolomite), — $\mathrm{MmnCO^3}$ (diallogite), — $\mathrm{ZznCO^3}$ (calamine), — $\mathrm{FfeCO^3}$ (spathic iron ore).
b. $\mathrm{NaNO^3}$, — $\mathrm{KNO^3}$. (Frankenheim.)

Group 12.

$\mathrm{All^2O^3}$, — $\mathrm{Ffe^2O^3}$, — $\mathrm{Ccr^2O^3}$.

Group 13.

Hyposulphates: $\mathrm{SsrS^2O^6.4H^2O}$, — $\mathrm{CcaS^2O^6.4H^2O}$, — $\mathrm{PpbS^2O^6.4H^2O}$. (Heeren.)

Group 14.

$\mathrm{CcaCl^2.3Cca^3P^2O^8}$ (apatite), — $\mathrm{PpbCl^2.3Ppb^3P^2O^8}$ (pyromorphite), — $\mathrm{PpbCl^2.3Ppb^3.As^2O^8}$ (mimetene).

Trimetric System.

Group 15.

Sulphur, — Iodine (?).

Group 16.

$\mathrm{As^2O^3}$, — $\mathrm{Sb^2O^3}$.

Group 17.

a. $CcaCO^3$ (arragonite),—$BbaCO^3$ (witherite),—$SsrCO^3$ (strontianite),—$PpbCO^3$ (cerusite),—$FfeCO^3$ (junkerite; Dufrénoy.)
b. KNO^3.
c. $(Ccu^2S.2PpbS).Sb^2S^3$ (bournonite; G. Rose).

Group 18.

a. $BbaSO^4$ (heavy spar),—$SsrSO^4$ (cœlestin),—$PpbSO^4$ (anglesite; Mitscherlich)
b. $KClO^4$,—$KMmnO^4$,—NH^4ClO^4,—$(NH^4)MmnO^4$. (Mitscherlich.)

Group 19.

a. Na^2SO^4,—Na^2SeO^4,—Ag^2SO^4,—Ag^2SeO^4. (Mitscherlich.)
b. $BbaMmn^2O^8$. (Mitscherlich.)

Group 20.

a. K^2SO^4,—K^2SeO^4,—K^2CcrO^4,—K^2MmnO^4. (Mitscherlich.)
b. $(NH^4)^2SO^4.H^2O$. (Mitscherlich.)

Group 21.

a. $MmgSO^4.7H^2O$,—$ZznSO^4.7H^2O$,—$NniSO^4.7H^2O$,—$MmgSeO^4.7H^2O$,—$ZznSeO^4.7H^2O$. (Mitscherlich.)
b. Sb^2S^3 (v. Kobell),—As^2S^3.

Group 22.

$NaPO^3.2H^2O$,—$NaAsO^3.2H^2O$. (Mitscherlich.)

Monoclinic System.

Group 23.

a. Sulphur.—*b.* $KHSO^4$,—$KHSeO^4$. (Mitscherlich.)

Group 24.

$CcaSO^4.2H^2O$,—$CcaSeO^4.2H^2O$ (Mitscherlich),—$FfeSO^4.2H^2O$. (Graham.)

Group 25.

$MmgSO^4.7H^2O$,—$ZznSO^4.7H^2O$,—$CcoSO^4.7H^2O$,—$NniSO^4.7H^2O$,—$FfeSO^4.7H^2O$,—$MmgSeO^4,7H^2O$,—$CcoSeO^4.7H^2O$. (Mitscherlich.)

Group 26.

$FfeSO^4.6H^2O$,—$CcoSO^4.6H^2O$,—$MmnSO^4.6H^2O$,—$CcoSeO^4.6H^2O$. (Mitscherlich.)

Group 27.

$MmgK^2S^2O^8.6H^2O$,—$Mmg(NH^4)^2S^2O^8.6H^2O$,—and similar double salts containing calcium, nickel, cobalt, iron, manganese, zinc, and copper.

Group 28.

$Na^2SO^4.10H^2O$,—$Na^2SeO^4.10H^2O$,—$Na^2CcrO^4.10H^2O$. (Mitscherlich.)

Group 29.

$(NH^4)^2HPO^4$,—$(NH^4)^2HAsO^4$. (Mitscherlich.)

Group 30.

$Na^2HPO^4.12H^2O$,—$Na^2HAsO^4.12H^2O$. (Mitscherlich.)

Group 31.

a. $Na^2B^4O^7.10H^2O$ (borax). *b.* $(Cca; Mmg)SiO^3$ (augite).

Triclinic System.

Group 32.

$MmnSO^4.4H^2O$,—$MmnSeO^4.4H^2O$,—$ZznSeO^4.4H^2O$,—$CcoSeO^4.4H^2O$. (Mitscherlich.)

Group 33.

$CcuSO^4.5H^2O$,—$CcuSeO^4.5H^2O$,—$MmnSeO^4.5H^2O$. (Mitscherlich.)

Bodies occurring more than once in this table are dimorphous or trimorphous.

To each group of isomorphous bodies in the dimetric, trimetric, monoclinic, and triclinic systems, there corresponds a particular pyramid with its prisms and domes, and to each group in the hexagonal system, a particular rhombohedron.

A perfectly exact accordance of the crystalline forms of two chemically different bodies, occurs perhaps only in the monometric system. Bodies of the same group which crystallise in other systems generally exhibit small differences in the corresponding angles. Thus, the angles of the terminal edges of the rhombohedrons of calcspar, diallogite, and the other isomorphous carbonates of group 11, exhibit the following differences:—

		R : R in terminal edges
Calcspar	$\mathrm{CcaCO^3}$ . . .	105° 5′
Dolomite	$\left.\begin{matrix}\mathrm{Cca}\\ \mathrm{Mmg}\end{matrix}\right\}\mathrm{CO^3}$ . . .	106° 15′
Diallogite	$\mathrm{MmnCO^3}$ . . .	106° 51′
Spathic iron	$\mathrm{FfeCO^3}$ . . .	107° 0′
Magnesite	$\mathrm{MmgCO^3}$ . . .	107° 25′
Calamine	$\mathrm{ZznCO^3}$ . . .	107° 40′.

In arragonite and the carbonates isomorphous therewith (group 17, *a*), the angles $\infty P : \infty P$ in the macrodiagonal principal section, and $\breve{P}\infty : \breve{P}\infty$ in the basal principal section, have the following values:—

		$\infty P : \infty P$	$\breve{P}\infty : \breve{P}\infty$
Arragonite . . .	$\mathrm{CcaCO^3}$	63° 44′	71° 33′
Witherite . . .	$\mathrm{BbaCO^3}$	61° 30′	73° 6′
Strontianite . .	$\mathrm{SsrCO^3}$	62° 44′	71° 48′
Cerusite . . .	$\mathrm{PpbCO^3}$	62° 46′	71° 47′.

Perfect equality in the corresponding angles of crystals is not always found, even in the monometric system. The simpler forms of that system, namely, the cube, octahedron, and rhombic dodecahedron, do not, of course, admit of any variation in the angles; but the remaining forms, which are expressed by formulæ containing finite numerical coefficients, viz. mOm, mO, $mO\infty$, and mOn, have different angles, according to the numerical values of those coefficients; and, consequently, crystals of two different substances crystallising in one of these forms may exhibit slight differences in their angles, as well as isomorphous crystals belonging to other systems. With regard to the three simpler forms of the monometric system, it may be observed that all bodies which crystallise in them may be regarded as isomorphous in a certain sense, inasmuch as all these forms are derivable one from the other; nevertheless, some bodies are more disposed to crystallise in one form than in the other, and a further distinction is afforded by the cleavage; thus, zinc-blende, ZznS, cleaves parallel to the faces of a rhombic dodecahedron; galena, PpbS, parallel to the faces of a cube. Such bodies, in spite of their similarity of form and atomic constitution, cannot be regarded as strictly isomorphous, at least in the same degree as NaCl and KCl, which agree in the direction of their cleavage as well as in their form.

From the similarity of form of two compounds, the isomorphism of certain of their constituents may often be inferred. If a compound, $a + b + c$, is isomorphous with another, consisting of $a + b + d$, it may be concluded that c is isomorphous with d. For example, the isomorphism of $\mathrm{K^2PptCl^6}$ and $\mathrm{K^2IrrCl^6}$, leads to the conclusion that platinum and iridium are isomorphous. In this manner, the isomorphism of the following groups of elements may be inferred:

1. *Monometric Metals and Metalloïds.* Carbon (diamond), phosphorus, potassium, sodium, titanium, cadmium, lead, iron, copper, silver, gold, platinum, palladium, iridium, tin, zinc (TABLE I, group 1, *a*),—manganese, calcium, lithium, ammonium, nickel, cobalt (1, *b*, and 1, *c*),—osmium (1, *i*).

2. *Hexagonal Metals.* Arsenic, antimony, tellurium, osmium, iridium, palladium, bismuth.

3. Sulphur, selenium (1, *b*),—chlorine, iodine, bromine, fluorine, cyanogen, arsenic (?) (1, *c*),—oxygen (1, *e*).

In like manner, the isomorphism of certain groups of elements may be inferred from that of compounds in which they may be supposed to exist; thus, from the isomorphism of the corresponding phosphates and arsenates, regarded as compounds of metallic oxides, with $\mathrm{P^2O^5}$ and $\mathrm{As^2O^5}$, *e. g.* $\mathrm{2Na^2O.H^2O.P^2O^5 + 24H^2O}$ and $\mathrm{2Na^2O.H^2O.As^2O^5 + 24H^2O}$, the isomorphism of phosphoric and arsenic anhydrides may be inferred.

The isomorphism of different elements and groups of elements is, however, most completely shown by their capability of replacing one another in composition in various proportions, and without any alteration of crystalline form. Thus, in the alums, whose general formula is $MR'''(SO^4)^2.12H^2O$, the monatomic radicle, M, may be composed of potassium, sodium, ammonium, &c., and the triatomic radicle, R, of aluminium, ferricum, manganicum, chromicum, &c., in the most various proportions, the form, all the while, remaining the same as that of common potash-alum, $KAll(SO^4)^2.12H^2O$. Numberless examples of this isomorphous replacement are found among natural minerals; indeed, it is but rarely that any mineral is found in which the principal constituents are not more or less replaced by isomorphous substances. Striking examples of it are afforded by the spinels (p. 397, and group 1, *g*, Table I, p. 424), and by the garnets (1, *l*, p. 424).*

Relations between Crystalline Form and Atomic Volume.—Complete isomorphism between two compounds implies the fulfilment of three conditions, viz.:

1. Similar atomic constitution.
2. Similar crystalline form.
3. Equal atomic volumes of the several constituent elements.

By the volume of an atom, we understand, as explained in the article ATOMIC VOLUME (i. 440), the space occupied by the solid atom itself, together with a portion of the space which separates it from the intervening atoms: that is to say, the size, or rather the radius, of the atom (regarded as spherical) is supposed to include half the distance which separates it from the contiguous atoms. The atomic volume of a substance, according to this definition, is proportional to its atomic weight divided by its specific gravity $\frac{a}{s}$. It is clear that equal numbers of atoms similarly disposed will not *necessarily* produce the same external form, unless the corresponding atoms in the two bodies are equal or at least proportional in volume.

Two or more bodies in which all three of the above conditions of equality are fulfilled, are isomorphous in the stricter sense. The fulfilment or non-fulfilment of all or some of these conditions gives rise to eight different cases of similarity or dissimilarity of constitution, which may be enumerated as follows:

	Crystalline form.	Atomic constitution.	Atomic volume.		
a.	equal	equal	equal	Isomorphous in the narrower sense Isotomous	Isomorphous in the wider sense
b.	equal	equal	unequal	Homœomorphous	
c.	equal	unequal	equal		
d.	equal	unequal	unequal		
e.	unequal	equal	equal	Heteromorphous	Anisomorphous in the wider sense
f.	unequal	equal	unequal		
g.	unequal	unequal	equal		
h.	unequal	unequal	unequal	Anisomorphous in the narrower sense; Anisotomous	

The following table exhibits the atomic volumes of a number of bodies arranged according to similarity of crystalline form and atomic constitution. The first column of figures headed $\frac{a}{s}$, gives the quotient of the atomic weight divided by the specific gravity (the atomic weights being those of the oxygen scale, O = 200); the second gives the atomic volumes referred to that of carbon 44, as unity; the third, headed "theoretical," shows what the value of $\frac{a}{s}$ would be in each case if it were an exact multiple of 44.

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* Compounds containing indefinite proportions of isomorphous elements are represented in this work by formulæ, in which the isomorphous elements are separated by semicolons: *e.g.* alum, in which the potassium is partly replaced by ammonium, is expressed by the formula, $(K; NH^4)All(SO^4)^2.12H^2O$. In many works such compounds are represented by formulæ like $\left.\begin{matrix}K\\NH^4\end{matrix}\right\}All(SO^4)^2.12H^2O$; but this is objectionable, since, according to ordinary usage, it would imply that the molecule contains an atom of potassium as well as an atom of ammonium, whereas the real meaning is that the potassium and ammonium are present in such quantities as together to make up a monatomic atom or molecule.

Table II.

Atomic Volumes of Isomorphous Bodies.

			Atomic volume.		
			$\frac{e}{s}$	44 = 1.	Theoretical.
	I. Elements.				
	a. Monometric.				
1	Carbon (Diamond)	C	44	1	44
2	Iron	Ffe	90	2	88
	Manganese	Mmn	88	2	88
	Nickel	Nni	88	2	88
	Cobalt	Cco	88	2	88
	Copper	Ccu	88	2	88
3	Platinum	Ppt	114	2½	110
	Palladium	Ppd	114	2½	110
	Osmium	Oss	114	2½	110
	Iridium	Irr	114	2½	110
	Rhodium (?)	Rrh	114	2½	110
	Titanium	Ti	112	2½	110
	Zinc	Zzn	116	2½	110
4	Lead	Ppb	228	5	220
5	Gold	Au	128	3	132
	Silver	Ag	130	3	132
6	Phosphorus	P	222	5	220
7	Sodium	Na	292	6¾	297
8	Potassium	K	583	13½	594
	b. Hexagonal.				
9	Arsenic	As	160	3¾	165
10	Antimony	Sb	240	5½	242
11	Bismuth	Bi	270	6¼	275
	c. Bodies probably crystallising in similar forms.				
12	Bromine	Br	326	7½	330
	Chlorine	Cl	320	7½	330
	Iodine	I	320	7½	330
	Cyanogen	Cy	315	7½	330
	II. Proto-chlorides, bromides, and iodides.				
	Monometric.				
13	Chloride of silver	AgCl	320	7½	330
	Chloride of sodium	NaCl	325	7½	330
14	Bromide of silver	AgBr	367	8¼	363
15	Chloride of ammonium	NH^4Cl	437	10	440
16	Chloride of potassium	KCl	481	11	484
17	Iodide of silver	AgI	522	12	528
18	Bromide of potassium	KBr	608	14	616
19	Iodide of potassium	KI	667	15	660
	III. Protoxides, Mm̈O.				
	Monometric.				
20	Magnesia	MmgO	156	3½	154
	Cupric oxide	CcuO	156	3½	154
21	Manganous oxide	MmnO	188	4	176
	Zinc-oxide	ZznO	180	4	176
22	Cadmium-oxide	CcdO	230	5	220
23	Lead-oxide	PpbO	306	7	308
24	Strontia	SsrO	330	7½	330
25	Baryta	BbaO	402	9	396
26	Silver-oxide	Ag^2O	352	8	352
27	Soda	Na^2O	278	6	264
28	Potash	K^2O	446	10	440

TABLE II.

Atomic Volumes of Isomorphous Bodies—continued.

			Atomic volume.		
			$\frac{a}{s}$	44 = 1.	Theoretical.
	IV. Proto-sulphides and Selenides.				
	Monometric.				
29	Manganese-blende	MmnS	272	6	264
30	Zinc-blende	ZznS	296	6½	286
31	Selenide of lead	PpbSe	406	9	396
	Galena	PpbS	386	9	396
32	Silver-glance	Ag^2S	432	10	440
	V. Dioxides.				
	Dimetric.				
33	Titanic anhydride	TiO^2	260	6	264
	Stannic anhydride	SnO^2	270	6	264
	VI. Sesquioxides.				
	a. *Monometric.*				
34	Antimonic oxide	Sb^2O^3	662	15	660
	Arsenious oxide	As^2O^3	664	15	660
	b. *Hexagonal.*				
35	Alumina	All^2O^3	362	8½	374
	Ferric oxide	Ffe^2O^3	372	8½	374
36	Chromic oxide	Ccr^2O^3	384	9	396
	VII. Carbonates.				
	a. *Trimetric.*				
37	Arragonite	$CcaCO^3$	426	10	440
38	Strontianite	$SsrCO^3$	512	11½	506
	Cerusite	$PpbCO^3$	516	11½	506
39	Witherite	$BbaCO^3$	576	13	572
	b. *Hexagonal.*				
40	Zinc-spar	$ZznCO^3$	352	8	352
	Magnesite	$MmgCO^3$	356	8	352
41	Spathic iron ore	$FfeCO^3$	378	8½	374
42	Diallogite	$MmnCO^3$	400	9	396
	Dolomite	$\left.\begin{matrix}\frac{1}{2}Mmg\\ \frac{1}{2}Cca\end{matrix}\right\}CO^3$	402	9	396
43	Calcspar	$CcaCO^3$	460	10½	462
	VIII. Nitrates.				
	a. *Hexagonal.*				
44	Nitrate of potassium	KNO^3	602	13½	594
45	Nitrate of sodium	$NaNO^3$	484	11	484
	b. *Monometric.*				
46	Nitrate of strontium	$SsrN^2O^6$	916	21	924
	Nitrate of lead	$PpbN^2O^6$	942	21½	946
47	Nitrate of barium	$BbaN^2O^6$	1024	23	1012
	IX. Magnesian Sulphates, $\overset{\prime\prime}{M}SO^4.7H^2O$.				
	Trimetric.				
48	Sulphate of nickel	$NniSO^4.7H^2O$	1724	39	1716
	Sulphate of zinc	$ZznSO^4.7H^2O$	1760	40	1760
	Sulphate of magnesium	$MmgSO^4.7H^2O$	1786	40½	1782

TABLE II.

Atomic Volumes of Isomorphous Bodies—continued.

			Atomic volume.		
			$\frac{a}{s}$	44 = 1.	Theoretical.
	X. Double Magnesian Sulphates, $M^2\overset{''}{R}(SO^4)^2.6H^2O$. *Monoclinic.*				
49	$(NH^4)^2Mmn(SO^4)^2.6H^2O$		2526	57½	2530
	$K^2Zzn(SO^4)^2.6H^2O$		2578	58½	2574
	$(NH^4)^2Nni(SO^4)^2.6H^2O$		2558	58½	2574
	$K^2Nni(SO^4)^2.6H^2O$		2578	58½	2574
	$(NH^4)^2Mmg(SO^4)^2.6H^2O$		2632	60	2640
	$K^2Ccu(SO^4)^2.6H^2O$		2604	59	2596
	$(NH^4)^2Ccu(SO^4)^2.6H^2O$		2840	64½	2838
	XI. Alums, $\acute{M}\overset{''}{R}(SO^4)^2.12H^2O$. *Monometric.*				
50	$KCcr(SO^4)^2.12H^2O$		3380	77	3388
	$KAll(SO^4)^2.12H^2O$		3472	79	3476
	$(NH^4)All(SO^4)^2.12H^2O$		3472	79	3476
	$NH^4Ffe(SO^4)^2.12H^2O$		3472	79	3476
	XII. Various Metallic Sulphides and Arsenides.				
	a. *Monometric.*				
51	Iron-pyrites	$FfeS^2$	292	6½	286
52	Cobalt-pyrites	Cco^2S^3	424	9½	418
	Smaltine	$CcoAs^2$	414	9½	418
53	Triarsenide of cobalt	$CcoAs^3$	530	12	528
54	Nickel-glance	$NniAs^2S^2$	658	15	660
	Cobaltine	$CcoAsS^2$	660	15	660
	b. *Trimetric.*				
55	Marcasite	$FfeS^2$	306	7	308
56	Arsenical pyrites	$Ffe^2As^2S^2$	692	16	704
57	Trimetric (native) sulphur		195	4½	198
58	Monoclinic (fused) sulphur		201·8	4½	198

A comparison of the numbers in this table leads to the following general conclusions.

1. Only those bodies which are bracketed together in the table can be regarded as strictly isomorphous, or isotomous; and even among these, there are some whose isotomy is doubtful, *e.g.* nitrate of strontium and nitrate of lead (44); magnesio-ammonic sulphate and cuprico-ammonic sulphate (49).

2. Many substances commonly regarded as isomorphous are in reality only homœomorphous, inasmuch as their atomic volumes differ considerably. Such is the case with phosphorus and arsenic; magnesia and manganous oxide; soda and silver-oxide; lead-oxide, baryta, and strontia; manganese-blende and zinc-blende; nitrate of potassium and nitrate of sodium. The atomic volumes of these homœomorphous bodies are, however, related to one another by simple proportions, as in the following examples:—

Sodium	1	Arsenic	3
Potassium	2	Phosphorus	4
Arsenic	2	Soda (anhydrous)	3
Antimony	3	Silver-oxide	4

3. Bodies which are isomorphous in the free state, are not always so in combination. Copper is isomorphous with iron, manganese, nickel, &c.; but many copper-salts are not isomorphous with the corresponding salts of the other metals just mentioned. Zinc, titanium, and platinum are isomorphous in the free state, but by no means in their salts. On the other hand, many bodies are isomorphous in their compounds, but homœomorphous, or even heteromorphous, in the free state: thus phosphorus and arsenic are heteromorphous in the free state, but isomorphous in their compounds; and manganese and zinc, arsenic and antimony, magnesia and manganous oxide, potassium and sodium, soda and silver-oxide, are homœomorphous in the separate state,

but isomorphous in some of their compounds. This apparently paradoxical relation may arise either from dimorphism—the substances in question crystallising in the free state in a form different from that which they assume in combination—or from variation of atomic volume. In fact, the atomic volume of a compound is, in nearly all cases, less than the sum of the atomic volumes of its elements in the free state, the condensation being greater as the affinity is stronger. Hence it may happen that elements whose atomic volumes in the free state are unequal, may assume equal volumes in combination, and therefore yield isomorphous compounds.

4. Bodies of different atomic volume often crystallise in the same form, and are capable of crystallising together. Gold and silver, whose atomic volumes are nearly as 1 : 2, crystallise together in very variable proportions; so likewise do chloride of sodium, chloride of ammonium, and iodide of potassium, whose atomic volumes are to one another as 3 : 4 : 6. It is only, however, in the monometric system that perfect similarity of crystalline form is exhibited by substances of different atomic volume; in crystals belonging to other systems, difference of atomic volume in bodies of similar atomic constitution, is always accompanied by a slight difference in the magnitude of certain angles, as may be seen by comparing the angles and atomic volumes of the several members of the calcspar and arragonite groups (pp. 427, 430), the obtuse terminal angles in the former, and the angles P∞ : P∞ in the latter diminishing as the atomic volume increases. This relation between atomic volume and crystalline form is further shown by the observation of Mitscherlich, that the angle of a rhombohedron of calc-spar diminishes when the crystal is heated: for the specific gravity is thereby diminished, and consequently the atomic volume increased.

5. An interesting example of homœomorphism is afforded by nitrate of potassium, which is dimorphous, having a rhombohedral form similar to that of calcspar, and a trimetric form like that of arragonite. Its angles in these two forms are as follows:

	Atomic volume.	Terminal angle of rhomb. (nearly).	
Hexagonal Nitre KNO^3	27	106° 30′	
		∞P	P∞
Trimetric Nitre KNO^3.	27	61·0′	70° 4′

In its rhombohedral form, this substance agrees very nearly with dolomite and diallogite, the terminal angles of which are 106° 15′ and 106° 51′ respectively, and whose atomic volumes are equal to 9: hence it appears that two substances whose atomic volumes are as 1 : 3 may crystallise nearly in the same form. Similar relations, though not quite so close, may be traced between the atomic volumes and crystalline forms of rhombic nitre and arragonite.

The relations between the atomic volumes and crystalline forms of different substances are, however, far from being established on a perfectly satisfactory basis; indeed the general conclusions of different observers relating to this subject are in some instances directly contradictory to each other: the discrepancies doubtless arise in many instances from the want of exact determinations of crystalline form, and more especially of specific gravity.

Schröder, to whose observations, together with those of Kopp, the results detailed in the preceding pages are mainly due, has recently made further experiments on the relations between chemical constitution and specific gravity, and has arrived at the following conclusions respecting the atomic volumes of isomorphous bodies. When two different elements or groups of elements, *A* and *B*, unite with other elements or groups of elements, *C*, *D*, *E*, &c., forming the compounds *AC* and *BC*, *AD* and *BD*, *AE* and *BE*, &c., belonging to the same type and isomorphous by pairs, the differences of the atomic volumes of *AC* and *BC*, *AD* and *BD*, *AE* and *BE*, &c., are always equal; but if the pairs of compounds thus formed are not isomorphous, or if they are isomorphous, but belong to different types, then the differences of atomic volume are unequal, and different from what they would be if the pairs were isomorphous or belonged to the same type. If bodies of equal atomic volume be denominated isosteric, and analogous pairs of compounds exhibiting equal differences of atomic volume, parallelosteric, the preceding law may be more shortly stated as follows:—*Pairs of compounds which are isomorphous and analogous are likewise parallelosteric.* This law has been confirmed by Tschermak. (Wien. Akad. Ber. xlv. [2] 603.)

Schröder further concludes that the volume of any element, which, in the isomorphous nitrates, chlorides, bromides, iodides or sulphides, is the greater of the two constituting a pair, is condensed in the isomorphous sulphates, carbonates, silicates, and aluminates, to a comparatively greater amount, so as often to become the lesser of the two. Thus the atomic volumes of chloride, bromide, and nitrate of potassium (calculated on the hydrogen-scale) of atomic weights, are greater by 2·7 to 2·5 than those of the corresponding ammonium salts, whereas that of sulphate of ammonium is greater by 2·5 than that of sulphate of potassium.

With regard to the elements, Schröder finds that isosterism is accompanied quite as frequently, if not more so, by heteromorphism as by isomorphism; but that elements whose atomic volumes are to one another as 1 : 2 (like silver and gold) are often isomorphous. In oxides and salts also, Schröder finds that isosterism is associated with isomorphism less frequently than with heteromorphism.

The relations between the atomic volumes and the proportions of the axes (which determine the angles) in series of homœomorphous bodies, are also, according to Schröder's recent observations, less constant than was formerly supposed. It is true that the limiting members of each series with regard to the proportions between the axes, are also the limiting members with regard to the atomic volumes; but the intermediate terms do not generally exhibit the regular relation between axial proportions and the atomic volumes which has been noticed in the calcspar and arragonite groups. According to Tschermak, on the contrary (Wien. Akad. Ber. xlv. [2], 603; Jahresber. 1862, p. 9), homœomorphous bodies of analogous composition form the same series with regard to their axial relations, as with respect to their atomic volumes. (Compare i. 449–452.)

Polymeric Isomorphism. This term is applied by Scheerer to express the fact that 1 at. of an element may in some cases be replaced by two or more atoms of another, or, generally, *m* atoms of one element by *n* atoms of another, or by a group of atoms of other elements, without essential alteration of crystalline form. Instances of this kind of isomorphism are afforded by the sulphides of lead and silver (PpbS and Ag^2S), by the sulphide and chloride of silver (Ag^2S and Ag^2Cl^2), by numerous isomorphous chlorides and cyanides, in which the single atom Cl and the group CN discharge equivalent functions; and by the isomorphous salts of potassium and ammonium, in which NH^4 is equivalent to K. Numerous other examples may be found amongst organic compounds: thus the acetate and butyrate of copper, $C^2H^3O^2Cu$, and $C^4H^7O^2Cu$, are isomorphous, and the sulphates of many organic bases, *e.g.* ethylamine, methylamine, conine, unite with sulphate of aluminium, forming alums isomorphous with common potash-alum.

Natural minerals likewise afford examples of this kind of isomorphism, to which attention has been particularly directed by Scheerer. Thus, certain varieties of augite and hornblende contain alumina, while others, which are free from alumina, contain a larger proportion of silica, the substitution taking place, according to Scheerer, in the proportion 1 at. All^2O^3 to 1 at. SiO^2 (or $3Al^2O^6$ to $2SiO^6$), but, according to Rammelsberg, in the ratio of $2All^2O^3$ to $3SiO^2$ (p. 169). Another instance is afforded by the minerals cordierite (dichröite), and aspasiolite, which are isomorphous and agree in composition, excepting that, according to Scheerer, 1 at. magnesia in the former is replaced by 3 at. water in the latter. According to the formulæ given by Rammelsberg, however (*Mineralchemie*, pp. 768, 834), viz.,

Cordierite, $6MmgO.6(All;\ Ffe)^2O^3.15SiO^2$.
Aspasiolite, $4MmgO.6(All;\ Ffe)^2O^3.15SiO^2.8H^2O$,

it appears that 4 at. water in the latter take the place of 1 at. magnesia in the former.

For a full development of the theory of polymeric isomorphism as applied to minerals, see Scheerer (Handw. d. Chem. iv. 170).—On isomorphism in general, see Mitscherlich (Ann. Ch. Phys. [2], xiv. 172; xix. 350; xxiv. 264 and 355).—Breithaupt. J. pr. Chem. iv. 249).—Persoz, Ann. Ch. Phys. [2]; lx. 119).—Brooke (Phil. Mag. [3], xii. 406).—Johnston (*ibid.* xii. 325 and 480; xiii. 405).—Schaffgotsch (Pogg. Ann. xlviii. 335).—H. Kopp (*ibid.* liii. 446).—Hankel (*ibid.* lv. 479).—Frankenheim (J. pr. Chem. xxvi. 257 and 263).—Wallmark (*ibid.* xxxi. 169).—Nicklès (Compt. rend. xxvii. 611).—Pasteur (*ibid.* xxviii. 477).—G. Rose (Pogg. Ann. lxxvi. 75; lxvii. 143).

ISONITROPHENIC ACID. See PHENIC ACID.

ISOPHANE. Syn. with FRANKLINITE (ii. 707).

ISOPRENE. C^5H^8.—A very volatile hydrocarbon, polymeric with caoutchin (i. 757), obtained, together with the latter and other less volatile products, by the dry distillation of caoutchouc and gutta percha. After repeated rectification over sodium, it boils between 37° and 38°, has a specific gravity of 0·6823 at 20°, and vapour-density = 2·40 obs.; 2·36 calc. After keeping for a month, it became thickened, and acquired a bleaching action, in consequence of the absorption of ozone: on subsequently distilling it, the ozone acted violently on the hydrocarbon, and the residue suddenly solidified to a white amorphous mass having the composition $C^{10}H^{16}O$. (Gr. Williams, Proc. Roy. Soc., x. 516.)

ISOPURPURIC ACID. *Picrocyamic acid.* $C^8H^5N^5O^6$. (Hlasiwetz, Ann. Ch. Pharm. cx. 289; Jahresber. 1860, p. 455. Bayer, Bull. Acad. roy. Belgique, [2] vii. No. 8.)—An acid, isomeric with purpuric acid, but, like the latter, not known in the free state. The potassium-salt is obtained by the action of cyanide of potassium on picric acid:

$$C^6H^3N^3O^7 + 3CNK + 3H^2O = C^8H^4KN^5O^6 + CO^2 + NH^3 + 2KHO.$$

When a solution of 2 pts. cyanide of potassium (prepared by Liebig's process, ii. 215), in 4 pts. water, warmed to about 60°, is mixed with a solution of 1 pt. picric acid in 9 pts. water, the mixture being constantly stirred, a strong odour of ammonia and hydrocyanic acid is given off, and the liquid solidifies on cooling to a soft crystalline pulp; and on straining this mass upon linen, pressing it between bibulous paper, heating and triturating the red-brown crystalline residue with a small quantity of water, then throwing it on a filter, washing it with cold water, again pressing, dissolving it in a large quantity of boiling water, and leaving the hot-filtered solution to crystallise, *isopurpurate of potassium* separates, as a metal-green film, and in brown-red crystalline scales, exhibiting a green colour by reflected light. It dissolves sparingly in cold, more easily in boiling water, imparting a very deep purple colour, and is precipitated from a concentrated solution by carbonate of potassium,—which circumstance may be taken advantage of in the preparation of the salt, if, in consequence of the presence of impurities, it does not separate spontaneously as above described. The salt dissolves also in dilute *alcohol*. When heated to about 215°, it decomposes, with somewhat strong detonation, slight appearance of fire, and formation of a grey cloud: it may also be exploded by contact with sulphuric acid. Its solution is precipitated by salts of barium, lead, mercury, and silver; not by those of calcium, strontium, copper, or zinc. The solution does not give the ordinary reactions of cyanogen.—The salt dried at 100° contains $C^8H^4KN^5O^6$.

The *ammonium-salt*, $C^8H^4(NH^4)N^5O^6$ (at 100°), separates in metallic-shining, dark-green crystals, on adding a solution of chloride of ammonium to a very concentrated solution of the potassium-salt. It is easily recrystallised, and then forms small wedge-shaped crystals, brown-red by transmitted and green by reflected light. It is very slightly soluble in cold water, more easily in boiling water, forming a deep-purple solution. When heated on platinum-foil, it deflagrates like gunpowder.

The *barium-salt*, $C^8H^4BaN^5O^6$ (at 100°), separates on adding chloride of barium to a solution of the potassium-salt, as a nearly cinnabar-coloured precipitate, sparingly soluble in cold water, perfectly soluble, with purple colour, in hot water. In the dry state it has a light-green metallic lustre, but when triturated becomes red again, and deflagrates with a dazzling green light.

On mixing the hot concentrated solutions of cyanide of barium and picric acid, the liquid acquires a blood-red colour, and deposits a dark-coloured precipitate which is resolved by hot water into a red-brown powder with green lustre, soluble in water, and a substance containing a large quantity of carbonate of barium, insoluble therein.

The *calcium-salt*, $2C^8H^4CaN^5O^6.3H^2O$, separates, after 24 hours, from a mixture of a hot-saturated solution of the ammonium-salt with chloride of calcium, in green metallic-shining needles, which give off their water at 140°.

Lead-salt, $C^8H^4PbN^5O^6$.—The solution of the potassium-salt is completely precipitated by neutral acetate of lead; the precipitate, which is at first brown red and very bulky, soon becomes dark violet-brown and pulverulent; it dissolves with purple colour in boiling water, and the solution deposits slender microscopic needles, which, after drying, are light brown-red with greenish iridescence, and detonate very sharply when heated. It is not completely decomposed by sulphydric acid, and on boiling the remaining mass with water, a yellowish-red solution is obtained, which deposits shining brown crystalline tufts having the composition of the original salt.

The *potassium-salt*, $C^8H^4KN^5O^6$ ($C^8H^2KN^4O^5$, according to Bäyer), has been already described.

The *silver-salt*, $C^8H^4AgN^5O^6$ (at 100°), separates from a solution of the potassium-salt, on addition of nitrate of silver, as a brown precipitate, which dries up to a dark-green mass possessing metallic lustre. It detonates when heated, and dissolves with purple colour in a large quantity of boiling water.

The *sodium-salt*, $C^8H^4NaN^5O^6$, is obtained, like the potassium-salt, by the action of cyanide of sodium on picric acid. It is dark-green with metallic lustre, dissolves in water much more easily than the potassium-salt, and is more difficult to crystallise: the solution is red.

The *strontium-salt* is obtained by adding nitrate of strontium to a solution of the potassium-salt, as a green, pulverulent, indistinctly crystalline precipitate, which deflagrates with a red flame when heated.

Hlasiwetz regards isopurpuric acid as dibasic, and the monometallic salts above described as acid salts. The neutral salts have not been obtained in definite form; but the solution of the monopotassic salt, mixed with caustic potash, acquires a dark-violet colour, and yields a precipitate which soon decomposes and turns brown. A similar change of colour, followed by rapid decomposition, is produced on triturating the barium-salt with baryta-water. All the salts are very much like the corresponding purpurates; the ammonium-salt, according to **Grailich's** determinations, exactly resembles purpurate of ammonium (*murexid*), in its crystalline form and optical properties.

ISOPYRE (from ἴσος, equal, and πῦρ, fire, because its appearance when fused is the same as in the natural state). A silicate of calcium, aluminium, and iron, found at St. Just, near Penzance, in Cornwall, in a quartzose granite, with tourmalin and tin ore; also in breccia, on the Calton Hill, Edinburgh. It bears considerable resemblance to obsidian, having a conchoïdal fracture, no cleavage, a greyish-black to velvet-black colour, and vitreous lustre. Specific gravity, 2·912; hardness 6 to 6·5, nearly equal to that of orthoclase. Melts before the blowpipe to a black magnetic globule. Contains, according to **Turner's** analysis (Ed. N. Phil. J. iii. 263), 47·69 silica, 13·91 per cent. alumina, 15·43 lime, 20·07 ferric oxide, and 1·94 cupric oxide (loss 1·56 per cent.), agreeing nearly with the formula $Ca^2O. Al^4O^3.3SiO^2$, which is essentially the same as that of labradorite; but part of the iron in the mineral appears to be in the state of protoxide, and as long as this amount remains undetermined, the formula cannot be fixed with certainty.

ISOTARTARIC ACID and **ISOTARTRIDIC ACIDS.** See TARTARIC ACID, DERIVATIVES OF.

ISOTRIBROMHYDRIN. Syn. with tribromide of allyl (i. 141).

ISOTEREBENTHENE. See TURPENTINE.

ITACOLUMITE. A laminated granular quartz-rock, in which diamonds are generally found: it probably owes its lamination to talc or mica. It occurs in the mines of Brazil and the Ural; also in Georgia and North Carolina, where a few diamonds have been found. (**Dana**, ii. 24.)

ITACONIC ACID. $C^5H^6O^4$.—An acid obtained, together with citraconic acid (i. 992), by the dry distillation of citric acid. It bears a close resemblance to citraconic acid, but differs from it in solubility and in its reactions with nitric acid and with bromine. It is prepared by heating citric acid in a retort by a spirit-lamp, care being taken that the heat is applied at the bottom, and not on the sides, as in the latter case a portion would be converted into citraconic acid. The distillation is continued until empyreumatic vapours appear. The oily distillate is then dissolved in six parts of boiling water, and evaporated to crystallisation: the crystals which are first formed consist of itaconic acid; citraconic acid, which is always formed at the same time, remains dissolved in the mother liquor. Frequently the distillate solidifies on cooling. In this case the crystals are pressed between bibulous paper on a plate at 100°, and then between paper moistened with absolute alcohol, and lastly recrystallised from water.

Itaconic acid is inodorous, and has a strongly acid taste: when crystallised from water, it has the form of a rhombic octahedron. It dissolves in 17 pts. of *water* at 20°, and is much more soluble at a higher temperature. It is soluble in *alcohol* and in *ether*. It melts at 161° to a colourless liquid which crystallises on cooling; when further heated, it decomposes into citraconic anhydride and water. Unlike citraconic acid, it does not yield mesaconic acid when treated with nitric acid. When treated with *bromine* and water, it takes up 2 at. bromine without evolution of hydrobromic acid, and forms an acid having the composition of dibromo-pyrotartaric acid, $C^5H^6Br^2O^4$, (**Kekulé**, Ann. Ch. Pharm. Supp. i. 338; ii. 111; **Cahours**, Ann. Ch. Phys. [3], lxvii. 129), and called ***itadibromosuccinic acid*** by **Kekulé**, ***dibromitaconic acid*** by **Cahours** (see PYROTARTARIC ACID, DERIVATIVES OF). Citraconic acid yields the same or an isomeric acid (**Cahours**). Itaconic acid treated with *sodium-amalgam* takes up 2 at. hydrogen and forms pyrotartaric acid, $C^5H^8O^4$ (**Kekulé**).

Itaconates. Itaconic acid is dibasic, forming acid salts, $C^5H^5MO^4$, and neutral salts, $C^5H^4M^2O^4$. The neutral itaconates of the alkali-metals do not crystallise. The *acid potassium*-salt is very soluble in water, and crystallises in lustrous laminæ. It is obtained by neutralising the acid with potash, adding a quantity of acid equal to that already taken, and evaporating to crystallisation. The alkaline salts are soluble, and give white precipitates with the soluble salts of lead, mercury, and silver.

Amides of Itaconic acid. The amides of itaconic acid are not known, excepting perhaps *itaconamic acid*, which appears to be formed by heating itaconate of ammonium to 190°, whereby a brownish acid mass is obtained which forms a very soluble salt with ammonium. But some of the corresponding phenylamine-compounds have been investigated by **Gottlieb** (Ann. Ch. Pharm. lxxvii. 215), to whose researches the reader is referred for further details.

Phenylitaconamide, $C^{17}H^{16}N^2O^2$, is derived from neutral citraconate of phenylamine by the loss of two atoms of water:

$$C^{17}H^{20}N^2O^4 = 2H^2O = C^{17}H^{16}N^2O^2.$$

It is obtained by heating itaconic acid with excess of phenylamine in a retort at a temperature a little above 180°. It crystallises in large thin plates with a pearly lustre.

Phenylitaconamic acid, $C^{11}H^{11}NO^{3}$, is derived from the acid itaconate of phenylamine by loss of water:

$$C^{11}H^{13}NO^{4} - H^{2}O = C^{11}H^{11}NO^{3}.$$

It is obtained by evaporating phenylamine to dryness with an excess of itaconic acid, and heating the residue a little above 100°. It forms large colourless needles, more soluble in alcohol than in water. Heated to 160° it is decomposed.

Itaconic Ether. $C^{9}H^{14}O^{4} = C^{5}H^{4}(C^{2}H^{5})^{2}O^{4}$. Itaconic acid is mixed with alcohol and hydrochloric acid, and the mixture distilled until about a third of the alcohol has passed over: water is then added to the residue, which separates the ether. It is a colourless, inodorous oil with a slight aromatic odour and bitter taste. It boils at 225°, but begins to decompose at this point. E. A.

ITTNERITE. A silicate occurring in monometric crystals, with dodecahedral cleavage, also granularly massive, in the dolerite of the Kaiserstuhl, near Freiberg; in basaltic dolerite at Sasbach; in phonolitic dolerite, with pyrites, titanic iron, and apatite, at Endingen. Hardness = 5·5. Specific gravity = 2·37 to 2·40. Colour dark-bluish or ash grey, or smoky grey. Lustre resinous. Translucent. Fracture imperfectly conchoïdal. When heated in a tube, it gives off a large quantity of water, and before the blowpipe melts easily, with strong intumescence and evolution of sulphurous anhydride, forming a blebby opaque glass. Forms a clear glass with borax. Gelatinises easily with acids.

The composition of the mineral is shown by the following analyses: *a.* by C. Gmelin (Schw. J. xxxvi. 74), *b.* by Whitney (Pogg. Ann. lxx. 442).

	SiO^{2}	SO^{3}	Cl	$Al^{4}O^{3}$	$Fe^{4}O^{3}$	$Ca^{2}O$	$Na^{2}O$	$K^{2}O$	Water and loss.*		
a.	34·02	2·86	0·73	28·40	0·61	7·26	12·15	1·56	10·76	=	98·35
b.	35·69	4·62	1·25	29·14	. .	5·64	12·57	1·20	9·83	=	99·94

* Including sulphur undetermined.

According to the latter analysis, ittnerite may be regarded as a mixture of hydrated sodalite and hauyne (p. 15). (Dana, ii. 319; Rammelsberg, *Mineralchemie*, p. 712.)

IWAARITE. A black mineral from Iwaara in Finland, which crystallises in monometric forms, melts before the blowpipe to a black glass, and, according to Thoreld, consists of silica, titanic acid, lime, and ferric oxide: perhaps identical with schorlamite. (Rammelsberg, *Mineralchemie*, p. 887.)

IXIOLITE. A variety of tantalite from Kimito in Finland, containing considerable quantities of manganese and tin.

IXOLITE. A fossil resin found in a bed of bituminous coal at Oberhart, near Gloggnitz. It is amorphous, with a fatty lustre and hyacinth-red colour, becoming yellowish when pulverised. It is subtranslucent in thin fragments. Fracture imperfectly conchoïdal in the purer varieties. Specific gravity = 1·008. Hardness = 1. Softens at 76°, but is still tenacious at 100°. (Haidinger, Pogg. Ann. lvi. 345.)

J

JADE. See NEPHRITE and SAUSSURITE.

JALAP. This name is applied to the roots and tubers of certain plants of the convolvulaceous order, which yield purgative resins. The true or officinal jalap consists of the tubers of *Convolvulus Schiedanus* (or *Exogonia purga*, according to Pereira), which contain a strongly purgative resin called convolvulin, $C^{31}H^{50}O^{16}$ (ii. 15), Kayser's *rhodeoretin*.

Spurious, woody or fusiform jalap, jalap-wood, or jalap-stalks (*Stipites Jalapæ*), the root of *Convolvulus orizabensis*, is sometimes mixed with genuine jalap. Its characteristic principle is jalapin, $C^{34}H^{56}O^{16}$ (Kayser's *pararhodeoretin*, p. 438), a resin homologous with convolvulin, and identical, or nearly so, with scammonin, the active principle of *Convolvulus Scammonia* (p. 438). The experiments of W. Mayer (Ann. Ch. Pharm. xcv. 161) seem to show that both convolvulin and jalapin exist in both kinds of jalap.

JALAPIC ACID. $C^{34}H^{60}O^{18}$? *Scammonic* or *Scammoninic acid.* (W. Mayer, Ann. Ch. Pharm. xcii. 115; xcv. 129. Spirgatis, *ibid.* cxvi. 289.)—An acid produced, with assimilation of water by dissolving jalapin in aqueous solutions of the alkalis or alkaline earths. Jalapin is heated with baryta-water to the boiling point, until the whole is dissolved, and acids no longer form a precipitate in the solution; the baryta is then removed by sulphuric acid; the excess of this acid by hydrate of lead; and the dissolved lead, by sulphydric acid. The filtrate boiled to remove the sulphydric acid, and evaporated, deposits jalapic acid, which, in case it has become coloured, may be decolorised by treatment with animal charcoal, or by boiling it with a little hydrate of lead, and subsequently passing sulphydric acid through the liquid.

Jalapic acid is a translucent, amorphous, shining, yellowish, brittle mass, which does not soften below 100°, and at about 120° melts to a turbid, very hygroscopic syrup. It has no smell, but an irritating sweetish taste (Mayer), or a sourish irritating taste, with bitter after-taste (Spirgatis). It has a strong acid reaction; dissolves very easily in *water*, easily also in *alcohol*, less easily in *ether*. It contains, according to the mean of Mayer's analyses, 54·4 per cent. carbon and 8·3 hydrogen; according to Spirgatis, 54·6 carbon and 8·2 hydrogen: hence Mayer deduces the formula $C^{68}H^{59}O^{35}$, requiring 54·6 carbon and 7·9 hydrogen; the formula above given, which requires 54·0 carbon and 8·0 hydrogen, is perhaps more probable.

Jalapic acid decomposes at about 130°; when heated on platinum foil, it burns with a bright sooty flame. When a concentrated aqueous solution is stirred for a long time with fuming *hydrochloric acid*, it splits up into jalapinol and glucose (Mayer):

$$2C^{34}H^{60}O^{18} \quad + \quad 7H^2O \quad = \quad C^{32}H^{62}O^7 \quad + \quad 6C^6H^{12}O^6.$$

The jalapic acid obtained from scammony forms jalapinolic acid, instead of jalapinol (Spirgatis; see p. 440). The same decomposition appears to be caused by emulsin (Mayer). Mayer obtained alphajalapie acid by boiling jalapic acid with dilute acids By *nitric acid* jalapic acid is converted into ipomæic and oxalic acids. When melted with *hydrate of sodium*, it gives off hydrogen, and forms jalapinolic and oxalic acids.

Jalapates. Jalapic acid unites with bases, forming salts in which 1, 2, and 3 at. hydrogen are replaced by the same number of atoms of metal: mixtures of these different salts are, however, very apt to form. It displaces carbonic acid from the carbonates of the alkalis and alkaline earths. Even when neutralised with an alkali, it gives no precipitate with any metallic salt, except basic acetate of lead. The jalapates are amorphous.

Barium-salts. The *monobarytic salt*, $C^{68}H^{118}BaO^{36}$, is obtained by mixing aqueous jalapic acid with a slight excess of baryta-water, removing the excess of baryta with carbonic acid, then warming and evaporating the filtrate. It resembles the tribarytic salt, and contains, according to Mayer's analysis, 49·7 per cent. C, 7·6 H, and 8·6 Ba, the above formula requiring 49·4 C, 7·1 H, and 8·3 Ba.

The *tribarytic salt*, $C^{34}H^{57}Ba^3O^{17}$, is prepared by boiling jalapin for 4 to 6 hours, with 2 pts. hydrate of barium and 4 pts. water (or mixing it with an equal weight of hydrate of barium, melted for half an hour in an air-bath, and then heated with water), and passing carbonic acid through the boiling solution, which is then filtered and evaporated down, and the residue dried at 100° in a current of air. It is an amorphous, neutral, slightly-coloured mass, having a slightly irritating, bitter-sweet taste. It melts at 100°, and decomposes with intumescence when strongly heated. It is soluble in water and alcohol, and is not decomposed by carbonic acid (Mayer, Spirgatis). It contains, according to Mayer, 42·1 per cent. C, 6·0 H, and 21·6 Ba, the preceding formula requiring 43·2 C, 6·0 H, and 21·8 Ba. [Mayer's formula, $C^{68}H^{56}Ba^3O^{36}$, requires 42·4 C, 5·9 H, and 21·3 Ba.]

A salt of intermediate composition, perhaps the *dibarytic salt*, appears also to be formed under certain circumstances (Mayer).

Jalapate of lead.—Recently precipitated hydrate of lead dissolves in boiling aqueous jalapic acid, forming an amorphous, easily soluble salt. When the aqueous acid is boiled for a long time with excess of hydrate of lead, a gummy, tumefied, basic salt is formed, which is insoluble in water, and very sparingly soluble in alcohol. The aqueous acid gives no precipitate with neutral acetate of lead, but copious white flakes with the basic acetate (Mayer, Spirgatis). Ammoniacal acetate of lead, or the basic acetate, throws down, from the aqueous acid, a flocculent precipitate, which may be purified by repeated solution in acetic acid, precipitation with ammonia, and washing. After being dried over oil of vitriol, it does not lose weight at 130° (Keller). It contains, according to Keller's analysis, 31·1 per cent. lead; the formula $C^{34}H^{57}Pb^3O^{18}$ requires 29·1 per cent. Keller's salt probably contained excess of base.

Alpha-jalapic acid. $C^{28}H^{50}O^{15}$. (W. Mayer, Ann. Ch. Pharm. xcv. 155.)—When dilute aqueous jalapic acid is boiled for not too long a time with hydrochloric or dilute sulphuric acid, one part of the jalapic acid is completely converted into jalapinol and sugar, another smaller part into alphajalapic acid, which, on cooling, separates out, with the jalapinol, as a soft, brown, semi-crystalline mass. By boiling this mass with baryta-water, removing the jalapinolate of barium which separates on cooling, and concentrating the mother-liquor, white silky needles of alphajalapic acid are obtained, while jalapinate of barium remains in solution. The needles are purified by recrystallisation from water; then dissolved in boiling water, and decomposed by acetic acid; and the alphajalapic acid, which crystallises out on cooling, is collected and purified by washing, recrystallising from water, acidulation with acetic acid, solution in alcohol, and precipitation with hot water.

Alphajalapic acid forms white, flexible needles, exhibiting a silky lustre under water, melting below 80° to a pale yellow thin oil, and forming a crystalline solid on cooling. It has no smell, but an irritating taste, with sweetish after-taste, and is feebly acid. It dissolves sparingly in cold, more freely in boiling *water*, easily in alcohol and in ether.

When the barium-salt (or the acid itself) is *heated*, it is decomposed, with frothing, and gives off a brown acid oil, which solidifies on cooling, partly in the crystalline form. When treated with *dilute acids*, or boiled with *nitric acid*, or melted with *hydrate of potassium*, it exhibits the same reactions as jalapic acid. In the decomposition with dilute acids, however, only 4 at. sugar are formed to 1 at. jalapinol, whereas jalapic acid (p. 437) yields 6 at. sugar:

$$2C^{28}H^{50}O^{13} + 5H^2O = C^{32}H^{62}O^7 + 4C^6H^{12}O^6.$$

Alphajalapate of barium, prepared as above, forms white, glittering, brittle, crystalline needles, having a sweetish irritating taste, and melting easily, without loss of water, to a thin oil, soluble in water and in alcohol. It contains 10·5 per cent. barium, corresponding with the formula $C^{28}H^{49}BaO^{13}$, which requires 10·4 per cent. barium.

JALAPIN. $C^{34}H^{56}O^{16}$. (J. Johnston, Phil. Trans. 1840, p. 342; Phil. Mag. [3], xvii. 183.—A. Kayser, Ann. Ch. Pharm. li. 101.—W. Mayer, *ibid.* xcv. 129.—*On Jalapin from scammony-resin:* Johnston, Phil. Trans. 1840, p. 340.—Fr. Keller, Ann. Ch. Pharm. civ. 63; further, with altered data, *ibid.* cix. 209.—Spirgatis, *ibid.* cxvi. 289.)

This substance (Kayser's *Pararhodeoretin*) occurs in the root-stalk of *Convolvulus* (or *Ipomœa*) *orizabensis*, the jalap-stalks or jalap-wood of commerce, and forms the principal portion (soluble in ether) of the jalap-resin prepared therefrom. [On the resin of tuberose jalap-root, see ii. 15.]

The resin of jalap-stalks has been examined also by Hänle (Repert. xlviii. 365), and Planche (J. Pharm. xxiv. 169). According to Weppen (N. Br. Arch. lxxxvii. 153), it resembles the resin of *Convolvulus arvensis*, which, like jalapin, assumes a fine purple-red colour with sulphuric acid, and is soluble in ether (contrary to the statement of Planche, J. Pharm. xiii. 165, who found it insoluble in ether). The same resin has been examined by Chevallier (J. Pharm. ix. 306). The resin of *Convolvulus Soldanella* appears, according to Planche, to be freely soluble in ether and alcohol, as also the portion of the tuberose jalap-root which is soluble in ether: both these resins are therefore, perhaps, jalapin.

Commercial scammony resin, from *Convolvulus Scammonia*, was described some years ago by Bouillon-Lagrange and Vogel; also by Planche (J. Pharm. xiii. 165; xviii. 183). Cl. Marquart (N. Br. Arch. vii. 248; x. 139) described the resin obtained from the root, and believed he had separated from it a vegetable base (*convolvuline*). Johnston recognised the similarity between scammony-resin and the resin of the jalap-stalks; Spirgatis showed that *scammonin*, the chief constituent of the former, is either identical with jalapin, or differs from it only in so far that, when decomposed by acids, it at once yields scammonolic (jalapinolic) acid; whereas jalapin, according to Mayer, when treated in a similar manner, yields at first jalapinol (p. 439). These statements are, perhaps, better founded than the contrary statements of Keller and Kosmann (p. 440).

According to Planche, the resin of *Convolvulus sepium*, and according to Boutron and Charlard, that of *Conv. Turpethum* (J. Pharm. viii. 131), are not soluble in ether, and may thus be distinguished from jalapin.

In what follows, the statements of Kayser and Mayer relate to jalapin from jalap stalks; those of Keller and Spirgatis, to that from scammony.

Preparation.—*a.* From commercial *Resina Jalappæ ex stipitibus.* To a solution of the resin in a large quantity of alcohol, water is added, until it becomes slightly turbid; the whole is repeatedly boiled with animal charcoal, and the still-coloured filtrate is precipitated by neutral acetate of lead and a little ammonia, which produces a small greenish-brown precipitate. The liquid is filtered, and the filtrate freed from lead by passing sulphydric acid through it, then heating and filtering; the alcohol is again distilled off, and the resinous residue repeatedly kneaded in boiling water, then dissolved in ether, from which it may be recovered by evaporation (Mayer). Or the alcoholic resin, after treatment with animal charcoal, is boiled for a long time with freshly-precipitated hydrated oxide of lead; the lead is separated from the filtrate by sulphydric acid; and the resin is three times separated by water from the alcoholic solution, then well boiled in water and dissolved in ether (**Mayer**). **Kayser** exhausts the root with alcohol; evaporates the tincture; washes the resinous residue with hot water, dissolves it in alcohol, and treats the solution with animal charcoal; distils off the alcohol; boils the residue again with water; and dries it over a water-bath. **Johnston** examined a resin that was obtained either by dissolving the commercial resin in ether and evaporating the solution; or by exhausting the ground root of commerce with hot alcohol, evaporating the brown tincture, and extracting the residue with ether; or by extracting chips of the root with cold alcohol, evaporating, boiling the residue in water, dissolving the resinous residue in ether, and evaporating the solution.

b. From Scammony.—Coarsely-powdered scammony is exhausted with cold alcohol (boiling, according to Keller); the tincture is diluted with water till it becomes turbid, decolorised by animal charcoal, and filtered; the greater part of the alcohol is distilled off; and the residue mixed with water is heated in a water-bath, till the whole of the alcohol is driven off, after which the resin is treated for a long time in a water-bath, with frequently-renewed hot water, and at last dried up. The residue may be dissolved in ether and recovered by evaporation. (**Spirgatis.**)

The jalapin (obtained according to *a* or *b*) still contains a small quantity of a volatile acid (valerianic acid, according to Keller), which cannot be completely removed even by very long washing. It betrays itself by the smell which the jalapin emits when it is converted by bases into jalapic acid, and the resulting solution supersaturated with a mineral acid. Keller regards this acid, the bulk of which passes off in the water used in washing the jalapin, as an essential product of the decomposition of scammony; whereas Mayer and Spirgatis regard it as a mere contamination.

Properties.—Jalapin is a colourless, amorphous resin, translucent when in thin plates; at 100° it becomes brittle, and may be rubbed down to a white powder. It soften at 123°, and melts at 150° to a transparent, colourless, or pale-yellow syrup. It is tasteless and inodorous; in alcoholic solution it gives a scarcely perceptible acid reaction (**Mayer, Spirgatis**). It is but slightly soluble in *water*, but dissolves very easily and without decomposition in *alcohol*, *wood-spirit*, *ether*, and *chloroform*. It dissolves also in *benzene*, *oil of turpentine*, and *petroleum*.

The composition of jalapin dried at 100°, or in a vacuum at common temperatures, is shown by the following analyses.

			Analyses.			
	Calculation.		Kayser.	Mayer.	Keller.	Spirgatis.
34 C . .	408	56·66	58·13	56·52	56·65	56·47
56 H . .	56	7·77	8·07	8·18	8·39	7·93
16 O . .	256	35·57	33·80	35·30	34·96	35·60
$C^{34}H^{56}O^{16}$	720	100·00	100·00	100·00	100·00	100·00

Johnston found in the resin obtained from jalap-stalks, 55·76 to 56·65 per cent., in scammony-resin 54·06 to 55·32 per cent. carbon. Keller gives the formula $C^{76}H^{67}O^{35}$.

Decompositions.—1. Jalapin *heated* above 127° gives off carbon and hydrogen in the form of a volatile compound, which contains less oxygen than the residual resin (**Johnston**). Jalapin which melts at 150°, becomes brown when further heated, and acquires a pungent empyreumatic odour (**Spirgatis**).—2. When heated on platinum-foil, it takes fire, burns with a bright sooty flame and empyreumatic odour, and leaves charcoal.—3. It dissolves slowly in cold strong *sulphuric acid*, the solution, in five or ten minutes, acquiring a beautiful purple or maroon-red colour, then becoming brown, and finally black. On standing, or after dilution, a brown resin or a brown tallowy body separates from the liquid, while sugar remains dissolved (**Kayser, Mayer, Spirgatis**).—4. By heating with dilute *mineral acids*, jalapin (even that which has been dissolved in alkalis and thereby converted into jalapic acid) is decomposed into jalapinol and sugar (**Mayer**). When jalapin from scammony is treated in the same way, jalapinolic acid is obtained in place of jalapinol (**Spirgatis**). Formation of jalapinol:

$$2C^{34}H^{56}O^{16} + 11H^2O = C^{32}H^{62}O^7 + 6C^6H^{12}O^6 \quad (\textbf{Mayer}).$$

Of jalapinolic acid:

$$C^{34}H^{56}O^{16} + 5H^2O = C^{16}H^{30}O^3 + 3C^6H^{12}O^6.$$

If pure jalapin (or pure jalapic acid) has been used, no other bodies are produced than those just mentioned (**Mayer, Spirgatis**). According to Keller, when a solution (alkaline or alcoholic?) of scammonin is treated with strong sulphuric acid or with hydrochloric acid gas, and then left to itself, three decomposition-products result, and the formation of a fourth (formic acid or formic aldehyde) appears probable from the formulæ. The products of this decomposition are—*a*. A *neutral body*, $C^{28}H^{26}O^4$, also separable by alkalis into scammonolic acid (jalapinolic acid), and an alcohol, $C^{28}H^{28}O^6$.—

b. Amylic aldehyde, which passes over as valerianic acid when scammony-resin is boiled with potash-ley, and then with dilute sulphuric acid.—*c.* A *carbo-hydrate*, $C^{12}H^{9}O^{9}$, which, however, is converted into sugar by simple boiling with dilute sulphuric acid. Keller gives the equation:

$$C^{76}H^{67}O^{36} = C^{28}H^{26}O^{4} + C^{10}H^{10}O^{2} + 3C^{12}H^{9}O^{9} + C^{2}H^{4}O^{2}.$$

But, according to Spirgatis, the neutral body *a* must be regarded as ethyl-scammonolic ether: moreover, the valerianic acid is obtained only from impure scammonin. Kosmann (J. Pharm. [3], xxxviii. 83), by boiling scammony-resin with dilute sulphuric acid, obtains sugar and his *scammoneol*, as a soft, yellowish-white substance, having a silky lustre and acid reaction, and separating from the hot alkaline solution on cooling. He calculates, according to Johnston's analysis of scammony-resin, the formula $C^{32}H^{52}O^{16}$ for scammonin, and so arrives at the equation of decomposition:

$$C^{32}H^{52}O^{16} + 5H^{2}O = 3C^{6}H^{12}O^{6} + C^{14}H^{26}O^{3}.$$

—5. When jalapin is dissolved in aqueous solutions of *caustic alkalis*, *ammonia*, or *baryta-water*, or in boiling *alkaline carbonates*, water is assimilated, and jalapic acid, soluble in water, is formed (Mayer, Spirgatis), probably thus:

$$C^{34}H^{56}O^{16} + 2H^{2}O = C^{34}H^{60}O^{18}.$$

Even the purest jalapin yields also traces of jalapinolic acid and a volatile acid, but no sugar (Mayer). When jalapin is melted with *hydrate of sodium*, hydrogen is given off, and jalapinolic and oxalic acids are formed (Mayer). Keller, by boiling scammonin with alcoholic potash, obtained dark flakes (on account of impurities in the scammonin, according to Spirgatis); and on subsequently adding water to the solution, the compound, $C^{26}H^{26}O^{2}$ or $C^{13}H^{26}O$, was precipitated in white flakes, while valerate of potassium remained in solution. The body, $C^{13}H^{26}O$, regarded by Keller as an alcohol, is likewise formed, on boiling commercial jalapin (obtained from the resin of jalap-stalks) or scammony with baryta-water, or solution of potash; it evaporates with the water, and separates in gelatinous flakes from the distillate. At 40° it melts to an oil, crystallises on cooling, and contains, on the average, 78 per cent. C, 14·12 H, and 7·88 O. Keller regards this body as a product of the decomposition of scammonin (or more exactly of the neutral body, $C^{28}H^{26}O^{4}$ or $C^{14}H^{26}O^{2}$; Spirgatis regards it as a mixture of resins, since the greater portion of it is obtained on distilling the impure resin with water.

6. By *nitric acid*, jalapin is at first decomposed into jalapinol and sugar, and these products, when further subjected to the action of the nitric acid, are converted into ipomæic and oxalic acids (Mayer). A small quantity of nitric acid does not colour jalapin; but, in presence of guaiac-resin, a green colour is produced (Bull, Spirgatis). —7. When *sulphurous anhydride* is passed through an ammoniacal alcoholic solution of scammony resin, silvery-shining plates are separated, containing perhaps an aldehyde in combination with acid sulphite of ammonium. (Keller.)

JALAPINOL. $C^{32}H^{62}O^{7}$. (W. Mayer, Ann. Ch. Pharm. xcv. 145.)—Jalapin and jalapic acid are resolved, by contact with mineral acids, slowly at ordinary, more quickly at elevated temperatures, into jalapinol and sugar (pp. 437, 439). Jalapinol and sugar were also produced, in one instance, when aqueous jalapic acid was left for 24 hours in contact with emulsion of almonds at 36° to 38°; whereas, in a second experiment, pure emulsin did not effect the decomposition, perhaps because the solution was too strongly heated.

To prepare jalapinol, a moderately concentrated aqueous solution of jalapic acid is mixed with half its bulk of fuming hydrochloric acid, and left to itself for days, or till the clear mixture has solidified to a thick crystalline pulp; and the product, after being washed on a filter with cold water, is repeatedly melted under warm water, and purified by recrystallisation from alcohol, with help of animal charcoal.

Jalapinol forms white, cauliflower-like crystals, which melt at 62° or 62·5°, and solidify at 59·5° to a hard, brittle, crystalline mass. It makes grease-spots on paper; is inodorous; has an irritating taste, and weak acid reaction. It is soluble in *alcohol* and in *ether*.

In contact with *caustic alkalis*, aqueous *ammonia*, or *baryta*, it is converted, with elimination of water, into a salt of jalapinolic acid:

$$C^{32}H^{62}O^{7} + 2BaHO = 2C^{16}H^{29}BaO^{3} + 3H^{2}O.$$

JALAPINOLIC ACID. $C^{16}H^{30}O^{3}$.—An acid produced—1. By treating jalapinol with caustic alkalis, or with baryta (Mayer).—2. By the action of melting hydrate of potassium on jalapin or jalapic acid (Mayer). Jalapin and jalapic acid, prepared from scammony, are resolved by mineral acids into jalapinolic acid and sugar. (Spirgatis.)

Preparation.—1. Jalapin is added gradually and by small portions to hydrate of sodium melted with ⅛th pt. of water (the mass then frothing up violently, giving off hydrogen and turning brown); the mixture is heated and stirred as long as hydrogen continues to escape; the crumbling light-yellow mass is dissolved in water after cooling; and the greater part of the alkali is neutralised with acid. The jalapinolate of sodium, which separates after some hours, is collected, washed, and decomposed by hot acidulated water; the separated acid is again repeatedly melted with pure water, then dissolved in alcohol and treated with animal charcoal; the somewhat concentrated filtrate is mixed with a large quantity of warm water; and the solid acid which separates on cooling is collected (Mayer). From the mother-liquor filtered from the jalapinolate of sodium, excess of acid still separates a small quantity of impure jalapinolic acid (Mayer).—2. The hot aqueous solution of jalapic acid (from scammony) is digested in the water-bath for a fortnight with dilute sulphuric acid; and the tallowy mass which separates on cooling, is freed from sulphuric acid by washing with hot water, and crystallised from ether with help of animal charcoal (Spirgatis).—3. Jalapin from scammony is added to boiling baryta-water; the liquid is heated till the whole is dissolved, and a sample of the filtrate is not rendered turbid, either by water or by hydrochloric acid; and the solution, after filtration, is mixed with one-third of its volume of fuming hydrochloric acid. The liquid becomes turbid in about 20 hours, and solidifies in the course of 10 days to a thick pulp, which is collected, washed with cold water, remelted with hot water, and recrystallised four or five times from aqueous alcohol.

Properties. Jalapinolic acid forms white tufts of needles, appearing under a magnifying power of 300, as thin 4-sided prisms. It melts at 64° or 64·5° (60° to 61°, according to Keller,) and solidifies at 61·5° or 62° (Mayer), at 50° (Spirgatis), to a white radio-crystalline, hard and brittle mass. It makes grease-spots on paper; is lighter than water; inodorous, but has an irritating taste and acid reaction (Mayer, Spirgatis). It is insoluble in *water*, but soluble in *alcohol* and in *ether*.

When *heated* above its melting point, it decomposes with intumescence, emitting a pungent odour which attacks the eyes and throat.—*Nitric acid* oxidises it to ipomæic acid and oxalic acid (Mayer, Spirgatis).

Jalapinolates. The acid is monobasic, the general formula of its neutral salts being $C^{16}H^{29}MO^{3}$.

Jalapinolate of Ammonium, $C^{16}H^{29}(NH^{4})O^{3}.C^{16}H^{30}O^{3}$.—By dissolving jalapinol or jalapinolic acid in aqueous ammonia, an opalescent liquid is obtained which gives off ammonia when evaporated, solidifies to a crystalline mass when concentrated to a certain point, but if completely evaporated, leaves an amorphous neutral jelly soluble in water. The crystals are grouped like cauliflower-heads, and when strongly magnified, appear as long colourless needles. (Mayer.)

Jalapinolate of Barium, $C^{16}H^{29}BaO^{3}$, is obtained by precipitating jalapinolate of ammonium with chloride of barium, or by boiling jalapinol or alcoholic jalapinolic acid with baryta, and crystallises out on cooling, in microscopic, thin, white, lustreless needles, melting to a colourless liquid when heated. It is nearly insoluble in cold, sparingly soluble in boiling water, more easily in boiling aqueous alcohol. (Mayer, Spirgatis.)

Jalapinolate of ammonium precipitates aqueous *chloride of calcium*.

Jalapinolate of Copper. a. *Basic*.—When a slightly alkaline aqueous solution of the ammonium-salt is precipitated with cupric acetate, and the precipitate is washed and dried at 100°, a dark blue-green, amorphous, very loose mass is obtained, which melts, without loss of water, to a dark green liquid, and solidifies to a translucent brittle mass. It is insoluble in water, nearly soluble in alcohol, contains at 100°, 18·75 per cent. cupric oxide, and is therefore $2C^{16}H^{29}CuO^{3}.CuHO$ (calc. 18·24 per cent. $Cu^{2}O$). (Mayer.)

b. *Neutral*.—$C^{16}H^{29}CuO^{3}$. A hot aqueous solution of jalapinolate of sodium forms with hot aqueous cupric sulphate, a green-blue precipitate, which dries up to a light blue-green amorphous powder, melting to a dark green liquid when heated. (Spirgatis.) It gave by analysis 13·24 per cent. $Cu^{2}O$, the formula requiring 13·28 per cent.

Jalapinolate of ammonium precipitates *iron-salts*.

Jalapinolate of Lead, $C^{16}H^{29}PbO^{3}$, is obtained by precipitating alcoholic jalapinolic acid mixed with a little ammonia, with neutral acetate of lead, and washing the white amorphous precipitate with dilute alcohol and water. It sinters together to an opaque mass at 120°. It is sparingly soluble in water and alcohol.

Jalapinolate of Potassium is obtained by dissolving jalapinol in boiling aqueous potash. The solution on cooling solidifies to a crystalline pulp, which, after washing, and recrystallisation from water or alcohol, forms slender, white, silky needles, melting without decomposition when heated. It is neutral, forms an opalescent solution with water, even when free alkali is present, and is soluble in alcohol.

Jalapinolate of Silver, $C^{16}H^{29}AgO^{3}$.—The alcoholic solution of the acid neutralised with ammonia is precipitated by a warm solution of nitrate of silver, in flakes which have a scarcely perceptible crystalline character. (Keller.)

Jalapinolate of Sodium, $C^{16}H^{29}NaO^3$, crystallises in slender dazzling-white tufts of needles, which form a turbid solution with a small quantity of hot water, a clear neutral solution with a larger quantity, and are likewise soluble in alcohol. (Spirgatis.)

Jalapinolic Ether, $C^{18}H^{34}O^3 = C^{16}H^{29}(C^2H^5)O^3$. *Scammonolic ether.*—When hydrochloric acid gas is passed into a solution of jalapinolic acid in absolute alcohol, and the resulting liquid is mixed with water, a yellow oil separates, which must be washed, after solidification, with cold alcohol, dissolved in boiling alcohol, mixed with carbonate of sodium, and after it has separated out on cooling, repeatedly precipitated from the alcoholic solution by water. It may also be obtained from scammony resin, by passing hydrochloric acid gas into the alcoholic solution. (Spirgatis.)

JALPAITE. A cupriferous silver-glance from Jalpa in Mexico. It has a blackish lead-grey colour, is malleable like ordinary silver-glance, and has a specific gravity of 6·877 to 6·890. According to an analysis by R. Richter, it contains 14·36 per cent. sulphur, 71·51 silver, 13·12 copper, and 0·79 iron, agreeing nearly with the formula, $\left.\begin{matrix}\frac{3}{4}Ag\\ \frac{1}{4}Cu\end{matrix}\right\}^2S$. (Breithaupt, Jahresber. 1858, p. 682.)

JAMAÏCINE. An alkaloïd said to be contained in the bark of *Geoffroya inermis*, a leguminous tree growing in Jamaica and in Surinam. (Hüttenschmidt, Geiger's Mag. Pharm. Sept. 1824.—Winckler, Pharm. Centr. 1840, p. 120.)

JAMESONITE. A sulphantimonite of lead occurring in trimetric crystals. $\infty P : \infty P = 101° 20'$ and $78° 40'$. Observed planes ∞P, $\infty\breve{P}\infty$. Cleavage basal, very distinct; parallel to ∞P and $\infty\breve{P}\infty$ less distinct. Sometimes capillary; also massive with columnar structure; particles delicate, straight and parallel or divergent. Hardness = 2 to 2·5. Specific gravity = 5·5 to 5·8 (Haidinger). Lustre metallic. Colour and streak steel-grey. Opaque. Sectile.

When heated in an open tube, it gives off dense white fumes of antimonious oxide; on charcoal before the blowpipe it decrepitates, fuses readily, and passes off almost wholly in fumes.

Analyses.—*a.* from Cornwall, mean of three analyses by H. Rose (Pogg. Ann. viii. 99).—*b.* from Estremadura, by Schaffgotsch (*ibid.* xxxviii. 403).—*c.* from Tuscany, by Bechi (Sill. Am. J. [2] xiv. 60).—*d.* from Arany, Idka, by Löwe (*Haidinger's Berichte*, i. 62).

	S	Sb	Bi	Pb	Fe	Cu	Zn	Ag	
a.	22·34	34·29	. .	39·94	2·64	0·18	trace	. .	= 99·39
b.	21·78	32·62	1·05	39·97	3·63	. .	0·42	. .	= 99·47
c.	20·53	32·16	. .	43·38	0·94	1·25	1·74	. .	= 100·00
d.	18·59	33·10	0·22	40·82	2·99	1·78	0·35	1·48	= 99·33

These analyses lead to the conclusion that Jamesonite is an isomorphous mixture of sulphantimonite of lead $2Pb^2S.Sb^2S^3$, with the corresponding compounds of iron (copper, zinc, and silver). Such a mixture of one molecule of the iron-salt and three molecules of the lead-salt, viz. $2Fe^2S.Sb^2S^3.3(2Pb^2S.Sb^2S^3)$ or $(FePb^3\overset{'''}{Sb}{}^4)^xS^5$ would contain 21·64 per cent. S, 32·55 Sb, 42·02 Pb, and 3·79 Fe.

Jamesonite occurs principally in Cornwall, associated with quartz and minute crystals of bournonite; occasionally also in Siberia, Hungary, Spain, and Brazil. (Dana, ii. 75; Rammelsberg, p. 68).

JAPONIC ACID. $C^{12}H^{10}O^5$.—An acid produced by exposing to the air a solution of catechin in caustic potash. The liquid slowly blackens, and on adding hydrochloric acid, a black precipitate of japonic acid is produced. The acid is soluble in water, but insoluble in alcohol. It forms with potash, a black salt which produces black precipitates with metallic solutions. (Svanberg, Ann. Ch. Pharm. xxiv. 215.)

JARGIONITE. A variety of galena, crystallised in octahedrons. Specific gravity 6·932.

JARGON. Syn. with ZIRCON.

JAROSITE. A native ferroso-potassic sulphate from Baranco Jaroso near Sierra Amagrera in Spain. Crystallises in yellowish rhombohedrons with basal cleavage. (Dana, ii. 389.)

JASPER. A sub-species of quartz of which the following varieties are enumerated by Jameson.

1. *Egyptian jasper*, which is red or brown. The first is flesh-red, blood-red, yellow and brown, in ring-shaped delineations; in roundish pieces, dull, with conchoïdal fracture. Feebly translucent on the edges. Hard; easily frangible. Specific gravity, 2·63. It is found imbedded in red clay-ironstone at Baden, and is cut into ornaments.

The *brown* variety has its various shades of colour disposed in concentric stripes, alternating with black stripes. It occurs in the sands of Egypt, in spheroïdal masses, with glimmering lustre. Fracture conchoïdal. Feebly translucent on the edges. As hard as horn-stone. Specific gravity 2·6. Infusible. It is cut into ornaments.

2. *Striped jasper.* Colours grey, green, yellow, red, arranged in stripes, in flamed or spotted delineations. Massive, in whole beds. Dull. Fracture conchoïdal. Opaque. Less hard than Egyptian jasper; rather easily frangible. Specific gravity 2·5. It occurs in secondary clay-porphyry in the Pentland hills, and near Friburg in Saxony. It receives a fine polish.

3. *Porcelain jasper.* Colours grey, blue, yellow, generally of one colour, or with clouded delineations. Massive, and cracked in all directions. Lustre glistening. Fracture conchoïdal. Opaque. Easily frangible, and not very hard. Specific gravity, 2·5, fuses into a white or grey glass. It is always found along with burnt clay and earth slags. According to Werner, it is slate-clay converted into a kind of porcelain, by the heat of a pseudo-volcano from beds of burning coal. It is found on the coast of Fifeshire, in Shropshire, and Warwickshire, and some parts of Germany, where immense beds of coal appear.

4. *Common jasper.* Colours red and brown. Massive. Lustre, from shining to dull. Fracture conchoïdal. Opaque. Hard in a low degree; rather easily frangible. Specific gravity 2·6. Infusible before the blowpipe, becoming at last white. It occurs principally in veins as a constituent of agate. It is found in the Pentland hills, and in trap and transition rocks in Ayrshire and Dumfriesshire.

5. *Agate jasper.* Colours yellowish- and reddish-white. Massive, dull. Fracture flat, conchoïdal. Opaque. Rather hard. It occurs in layers in agate-balls in many places. U.

The *iaspis* of the ancients, whence our word jasper is derived, appears to have included the green or blue variety, together with some other stones not of the jasper kind.

JATROPHA. A genus of euphorbiaceous plants, some of which contain intensely poisonous juices: the seeds of several species yield fixed oil.

The kernels of the seeds of *Jatropha Curcas* were found by Arnaudon and Ubaldini (Cimento, vii. 431) to contain 7·2 per cent. water, 37·5 oil, 55·3 sugar, starch, albumin, casein and inorganic matters. The kernels yielded 4·8 per cent. ash, and 4·2 per cent. nitrogen; the kernels and husks together, 6 per cent. ash and 2·9 per cent. nitrogen. The oil yielded by saponification, glycerin, and an acid which, as well as the unsaponified oil, produced octylic alcohol by distillation with hydrate of potassium.

The oil of the fruit of *Jatropha glauca* and of *J. glandulosa* is yellow, has a specific gravity of 0·963 and solidifies at 5°. (J. Lepine, J. Pharm. [3] xl. 16.)

The root of *Jatropha Manihot* contains a large quantity of starch, which when freed from the poisonous juice of the plant by washing and torrefaction, constitutes Brazilian arrow-root (i. 359.)

JEFFERSONITE. A dark-green, crystallised, foliated variety of augite, containing zinc, from Mine Hill, Franklin, New Jersey. Specific gravity 3·6. Formula $(Ca; Fe; Mg; Zn)^2SiO^3$.

JELLETTITE. An altered form of garnet, said to occur in rhombic prisms with angles of 60°, the supplement of which, 120°, is the angle of the rhombic dodecahedron. Specific gravity = 3·741. Hardness above 7. Occurs as a yellowish, slightly-greenish incrustation, and is compact in its texture. Composition, according to Wright (J. Geol. Soc. Dublin, v. 119), 38·09 SiO^2, 33·41 Fe^4O^3, 28·61 Ca^2O = (100·11), which if a small part of the iron is regarded as protoxide, gives the formula of garnet. (Dana, ii. 194).

JEFREINOFFITE or **JEWREINOWITE.** A variety of vesuvian from Finland, containing, according to Ivanhoff, 37·41 SiO^2, 34·20 Ca^2O, 20·00 Al^4O^3, 4·60 Fe^2O, 1·16 K^2O, and 1·70 Na^2O (= 99·07). It is usually yellowish-brown, but sometimes colourless. (Dana, ii. 506.)

JENKINSITE. Syn. with HYDROPHITE (p. 212).

JERVINE. An alkaloïd discovered by E. Simon (Pogg. Ann. xli. 569), in the root of white hellebore (*Veratrum album*) in which it exists, together with veratrine. It is extracted by mixing the alcoholic extract of the root with dilute hydrochloric acid and precipitating with carbonate of sodium. The precipitate is dissolved in alcohol, the solution decolorised with charcoal, and the alcohol removed by distillation. The greater part of the residue then solidifies in a crystalline mass, from which the veratrine, being uncrystallisable, may be almost entirely removed by submitting it to pressure, moistening the resulting cake with alcohol, and pressing again. In this manner jervine is obtained nearly pure. A further quantity may be obtained, in the form of sulphate, by evaporating to dryness the expressed liquid, which contains both jervine and veratrine, and treating the residue with dilute sulphuric acid, which takes up sulphate of veratrine, and leaves sulphate of jervine.

Jervine is colourless and crystalline; gives off 6·9 per cent. water of crystallisation (2 at.) at 100°, and melts at a higher temperature to a colourless oil, which decomposes when heated above 200°. It is insoluble in water, soluble in alcohol, very sparingly soluble in ammonia.

According to Will's analysis (Ann. Ch. Pharm. xxxv. 116), it contains 74·91—74·55 per cent. carbon, 9·57—9·74 hydrogen, and 5·38 nitrogen, whence Will deduced the formula $C^{60}H^{45}N^{2}O^{5}$ for which Gerhardt substituted $C^{60}H^{46}N^{2}O^{6}$ or $C^{30}H^{46}N^{2}O^{3}$ (calculation 74·7 per cent. C, 9·5 H, 5·7 N, and 10·1 O).

Jervine gives off ammonia when fused with *potash*.

Acetate of jervine is soluble in water. The *sulphate*, *nitrate*, and *hydrochlorate* are very sparingly soluble in water and in mineral acids. The *chloroplatinate* forms light yellow flakes which give by analysis 14·55—14·33 per cent. platinum, the formula $C^{30}H^{46}N^{2}O^{3}.HCl.PtCl^{2}$ requiring 14·3 per cent.

JET. A variety of bituminous coal, resembling cannel coal, but blacker, and with a stronger lustre. Specific gravity 1·3. It occurs, together with lignite, in beds, in floetz, trap, and limestone rocks, and in bituminous shale. It is found on the coast of Whitby, in Yorkshire, in the Isles of Skye and Faroe, in Hessia, Bavaria, Bohemia, and Styria. It is used for fuel and for making various ornamental articles.

It is the *Gagates* of Dioscorides and Pliny, a name derived from the river Gagas, in Syria, near the mouth of which it was found. U.

JEWREINOWITE. Syn. with JEFREINOFFITE.

JOHANNITE. Native uranous sulphate. See URANIUM.

JOHNITE. Syn. with TURQUOIS.

JUGLANDIN. A substance contained in the juice expressed from the green shell of the walnut (*Juglans regia*). The fresh juice is nearly limpid, has a rough bitter taste, turns brown rapidly in contact with the air, and then loses its strong taste. By prolonged contact with the air, it deposits brown tasteless flocks, insoluble in water and alcohol, the juice at the same time losing its bitterness. The fresh juice reduces iron-salts; the browned juice, when mixed with potash, precipitates ferrous sulphate, losing its colour at the same time. With nitrate of silver it forms a precipitate which blackens rapidly, and contains metallic silver.

The extract of green walnut-shells consists of impure juglandin. It is used as a remedy in cutaneous and scrophulous diseases, also for dyeing the hair black. (*Gerh. Traité*, iv. 307).

JUNIPER. The berries of the juniper (*Juniperus communis*), which are used for flavouring gin, and in the form of aqueous decoction, also in medicine as a diuretic, contain, according to Trommsdorff, 1·0 per cent. essential oil of juniper, 4·0 wax, 10·0 resin, 33·8 sugar, together with acetate and malate of calcium, 7·0 gum and vegetable salts, 35·0 woody fibre, and 12·9 water.

The *essential oil of juniper*, obtained by distilling the berries with water, has the composition and vapour-density of oil of turpentine ($C^{10}H^{16}$); boils at 160°; turns the plane of polarisation to the left, but less strongly than oil of turpentine. It is very little soluble in alcohol of ordinary strength. It does not form a solid camphor with hydrochloric acid; but after the complete absorption of the gas, a liquid is formed which appears to contain $3C^{10}H^{16}.2HCl$.

The old and moist essence deposits crystals which appear to be identical with hydrate of turpentine. It is acid and contains formic acid.

By distilling unripe juniper-berries with salt-water, Blanchet obtained another oil, which boiled at 205°, but appeared to have the same composition as that just described. (*Gerh. Traité*, iii. 637.)

JUNKERITE. Spathic iron ore.

JURINITE. Syn. with BROOKITE.

K

KÆMMERERITE. A variety of pyrosclerite containing a considerable quantity of chromium. (See PYROSCLERITE.)

KÆMPFERIDE. A substance contained in the root of *Kæmpferia Galanga*. It may be extracted by ether, together with a brown, viscid, aromatic substance, which may be removed by dissolving the product several times in alcohol, the brown substance separating first when the solution is left to evaporate.

Kæmpferide crystallises in yellowish nacreous laminæ, without taste or smell. It melts at a temperature above 100°, dissolves in 25 pts. of ether at 15°, is less soluble in alcohol, and nearly insoluble in water. It dissolves in warm acetic acid, and the solution yields with ammonia a precipitate soluble in excess of that reagent. Sulphuric acid imparts to it a fine bluish-green colour. Caustic potash dissolves it with yellow colour; carbonate of potassium with effervescence.

Kæmpferide gave by analysis (calculated with the old atomic weight of carbon) 65·3 per cent. C, 4·3 H and 30·4 O. (Brandes, Ann. Ch. Pharm. xxxii. 312.)

KALISACCHARIC ACID. Syn. with Glucic Acid (ii. 848.)

KALYPLOTITE. A name given by Shepard (Sill. Am. J. [2], xii. 210) to some small black-brown crystals from Haddam, Connecticut, regarded by him as a new mineral. Dana, however, regards them as garnets.

KAMALA. A substance obtained from the fruit of *Rottleria tinctoria*, and used as an anthelmintic (see Rottleria).

KANEITE. Arsenical Manganese. (See Manganese.)

KAOLIN. The Chinese name of porcelain clay (i. 1024).

KAPNITE. A variety of calamine containing more than 15 per cent. of ferrous oxide. The angle of the rhombohedron R : R is 107° 7 (Breithaupt).

KARELINITE. An oxysulphide of bismuth occurring, together with telluric silver, in the Sawodinsk mine in the Altaï. It forms crude lumps, having a metallic aspect, a decidedly crystalline fracture, with prevailing cleavage in one direction, strong metallic lustre on the fractured surface, and lead-grey colour. Hardness = 2; specific gravity = 6·60. On treating the pulverised mineral with hydrochloric acid, a small quantity of admixed bismutite (i. 597) dissolves and pure karelinite remains undissolved. The latter heated in a test-tube gives off sulphurous anhydride, but no free sulphur, and forms a grey slag, from which globules of metallic bismuth ooze out; heated in an open tube, it also gives off sulphurous anhydride, and leaves a metallic regulus surrounded by a brown easily fusible oxide. Nitric acid easily decomposes the mineral, with separation of sulphur. The mineral gives by analysis 91·26 per cent. bismuth, 3·53 sulphur, and 5·21 oxygen, agreeing with the formula Bi^4SO^3 or $Bi^2S.Bi^2O^3$. (R. Hermann, J. pr. Chem. lxxv. 448.)

KARPHOLITE. See Carpholite (i. 806).

KARPHOSIDERITE. See Carphosiderite (i. 807).

KARSTENITE. Syn. with Anhydrite (i. 295).

KAWA-ROOT. The root of *Piper methysticum* (Forster). When dried between 110° and 120°, it leaves a residue amounting to 85 per cent.: after exhaustion with alcohol and with water, it leaves 75 per cent. of residue containing 26 pts. woody fibre and 49 starch. By exhausting the root with alcohol of 80 per cent. an extract having a peculiar smell and taste is obtained, the solution of which in warm alcohol deposits needle-shaped crystals, while a resin remains dissolved.

The crystalline substance called methysticin, forms, when purified by repeated crystallisation, small white silky needles, destitute of taste and smell. It is insoluble in water, sparingly soluble in cold alcohol and ether; reacts neutral; melts at 130°, and decomposes at a stronger heat; is dissolved by nitric acid with orange-yellow colour, by pure sulphuric acid with violet colour. It yields by analysis 62·03 per cent carbon, 6·10 hydrogen, and 1·12 nitrogen.

The resin kawin, contained, together with myristicin, in the alcoholic extract of the root, is a soft greenish-yellow substance, which has a strong aromatic taste and odour, melts at 50°, decomposes at a stronger heat, and produces a deep red colour with sulphuric acid. 100 pts. of kawa-root contain 15 pts. water, 26 woody fibre, 49 starch, 1 methysticin, 2 acrid aromatic resin, 3 extractive and gummy matter, 1 chloride of potassium, and 3 magnesia, silica, alumina, and ferric oxide. (Gobley, J. Pharm. [3], xxxvii. 19.—O'Rorke, Compt. rend. l. 498.)

KAWAIN. A crystallisable non-azotised substance, from kawa-root; it contain 65·85 per cent. carbon and 5·64 hydrogen. (Cuzert, Compt. rend. l. 436; lii. 206.)

KAWIN. The resin of kawa-root. (See above.)

KEDRIA TERRESTRIS. Barbadoes tar. (See Bitumen.)

KEILHAUITE. Syn. with Yttrotitanite.

KELP. Incinerated sea-weed. (See Sea-weed.)

KERAMOHALITE. A hydrated sulphate of aluminum from near Königsberg in Hungary, having the same composition as alunogen (i. 161). It occurs in crystalline crusts, and six-sided tables of the monoclinic system, with two angles of 92°, and four of 134°. Specific gravity = 1·6 to 1·7. Contains 14·30 per cent. alumina, 2·15 ferrous oxide, 36·75 sulphuric anhydride, 44·60 water, and 2·01 insoluble matter (= 99·81), agreeing approximately with the formula $Al^4(SO^4)^6.18H^2O$.

KERAPHYLLITE. Syn. with Carinthin (i. 804).

KERARGYRITE or *Horn-silver.* Native chloride of silver (See Silver).

KERASITE, *Cerasine,* or *Horn-lead.* A native compound of chloride and carbonate of lead. (See Lead.)

KERATE. Syn. with Kerargyrite.

KERMES (*Coccus ilicis,* Lin.) is an insect found in many parts of Asia, and the south of Europe. On account of their figure, these insects were a long time taken for the seeds of the tree on which they live: whence they were called *grains of kermes.* They also bore the name of vermillion.

To dye spun worsted with kermes, it is first boiled for half an hour in water with bran, then for two hours in a fresh bath with one-fifth of Roman alum and one-tenth of tartar, to which *sour water* is commonly added; after which it is taken out, tied up in a linen bag, and carried to a cool place, where it is left some days. To obtain a full colour, as much kermes as equals three-fourths, or even the whole of the weight of the wool, is put into a warm bath, and the wool is put in at the first boiling. As cloth is more dense than wool, either spun or in the fleece, it requires one-fourth less of the salts in the boiling, and of kermes in the bath.

The colour that kermes imparts to wool has much less bloom than the scarlet made with cochineal; whence the latter has generally been preferred, since the art of heightening its colour by means of solution of tin has been known. U.

KERMES, MINERAL. Amorphous trisulphide of antimony. (See Antimony, Sulphides of, i. 330.)

KERMESITE or **KERMESOME.** *Red Antimony. Antimony-blende. Pyrantimonite. Pyrostilbite. Rothspiessglanzerz.*—A native oxysulphide of antimony, occurring in monoclinic crystals, cleaving parallel to the base; usually in tufts of capillary crystals, consisting of elongated, slender, six-sided prisms. Hardness = 1 to 1·5. Specific gravity = 4·5 to 4·6. Lustre, adamantine, inclining to metallic. Colour, cherry-red. Streak, brownish-red. Feebly translucent. Sectile. Thin leaves slightly flexible. Contains 74·45—75·66 antimony, 5·29—4·27 oxygen, and 20·49 sulphur (H. Rose, Pogg. Ann. iii. 453), answering to the formula Sb^2OS^2 or $Sb^2O^3.2Sb^2S^3$. Before the blow-pipe on charcoal, it fuses readily, and is at last entirely volatilised. In nitric acid it becomes covered with a white coating.

This mineral, which results from the alteration of native sulphide of antimony, occurs in veins in quartz, accompanying grey and white antimony, at Malaekza near Posing in Hungary, at Bräunsdoff near Freiberg in Saxony, and at Allemont in Dauphiné. (Dana, ii. 141.)

KEROLITE. See Cerolite (i. 836).

KETONES. See Acetones (i. 31).

KHAYA. The bark of the *Caïl-cedra* (*Khaya senegalensis* or *Swietenia senegalensis*), used in Senegal as a remedy against fever, contains a bitter principle, caïlcedrin, together with green fat, red and yellow colouring matter, gum, starch, a waxy substance, woody fibre, sulphate and phosphate of calcium, and chloride of potassium. Caïl-cedrin, which may be extracted from the concentrated aqueous extract of the bark by chloroform, is a resinous mass containing 64·9 per cent. carbon, 7·6 hydrogen, and 27·5 oxygen. (Caventou, J. Pharm. [3] xvi. 355; xxxiii. 123.)

KIBDELOPHANE or *Axotomous Iron ore.* A variety of titaniferous iron, occurring sometimes in crystals, but usually massive, or in thin plates or laminæ. R : R = 85° 19′. Hardness = 5 to 5·5. Specific gravity = 4·661 (Mohs); 4·723 to 4·735. (Breithaupt.)

KIFFEKILL. See Meerschaum.

KIESERITE. A name applied by Reichardt (Arch. Pharm. [2], ciii. 346) to a sulphate of magnesium, occurring in the shaft of the Stassfurth salt-mine near Magdeburg, and containing, according to his analysis, 21·66 per cent. Mg^2O, 43·05 SO^3, and 34·56 water (= 99·27), agreeing approximately with the formula $2Mg^2SO^4.3H^2O$.—Siewert (Zeitschr. f. d. ges. Naturw. xvii. 49) found in a much harder opaque specimen (mean) 28·56 Mg^2O, 58·94 SO^3, and 13·47 H^2O), together with from 0·26 to 0·66 of matter insoluble in nitric acid), answering to the formula $2Mg^2SO^4.H^2O$. Similar results were obtained by B. Leopold (*ibid.* p. 51), who also found that the salt contained from 0·5 to 1·2 per cent. of an insoluble borate (see SULPHATES); also previously by Rammelsberg (*Mineralchemie*, p. 264).

KILBRICKENITE. Geocronite from Kilbricken, Clare County, Ireland. (See GEOCRONITE, ii. 831.)

KILLAS. The Cornish miners' name for clay-slate.

KILLINITE. A mineral having the appearance of spodumene, found at Killiney Bay, near Dublin. According to Mallet, it affords by cleavage a prism of 135°, which is very nearly the angle between the diagonal and prismatic cleavages of spodumene, both of which are perfect. Hardness = 4. Specific gravity = 2·56. Lustre, vitreous, weak. Colour, greenish-grey, brownish, or yellowish. It has been analysed by Lehunt, Blythe, Mallet, and Galbraith (Dana, ii. 170; Rammelsberg's *Mineralchemie*, p. 837.)

SiO^2	Al^4O^3	Fe^2O	Ca^2O	Mg^2O	Mn^2O	K^2O	Li^2O	H^2O			
49·08	30·60	2·27	0·68	1·08	—	6·72	—	10·00	=	100·43	Lehunt.
47·93	31·64	2·33	0·72	0·46	1·25	6·06	—	10·00	=	99·80	Blythe.
52·89	33·24	3·27	1·45	—	—	4·94	0·46	3·67	=	99·92	Mallet.
50·45	30·13	3·53	—	1·09	—	4·81	Na^2O 0·95	7·58	=	98·54	Galbraith.
50·11	29·37	2·23	0·34	1·03	—	6·71	Li^2O 0·60	8·03	=	98·42	"

According to Rammelsberg, this mineral, and likewise pinite, gieseckite, gigantolite, iberite, and liebenerite, which are of somewhat similar constitution, are not definite compounds, but products of decomposition intermediate between an original mineral and mica, which often adheres to and partly penetrates their mass.

KINIC ACID. Syn. with QUINIC ACID.

KINO. This name is applied to four different drugs, bearing considerable resemblance to catechu, and consisting of dry brown lumps or grains, having a more or less astringent taste. Their aqueous extracts form green precipitates with ferric salts. The four varieties of kino are African kino, also called *Gummi gambiense*, or *G. Gambia*, from the *Pterocarpus erinaceus* (Lam.); Asiatic kino, from *Pterocarpus Marsupium*; New Holland kino, from *Eucalyptus resinifera* (white); and American kino, from *Coccoloba uvifera* (L.).

According to Vauquelin, African kino consists of 75 pts. tannin and peculiar extractive matter, 24 pts. red gum, and 1 pt. fibrin.

Kino is used in medicine as an astringent like catechu. (Handw. d. Chem. iv. 352.)

KINONE. Syn. with QUINONE.

KINOVOUS ACID. $C^{24}H^{38}O^5$ (?). An acid obtained, together with several other products, from the needles of *Pinus sylvestris*. (For the mode of preparation, see PINE-RESINS.) It is a white or slightly yellow brittle mass, converted by trituration into a strongly electric powder. The silver-salt contains 74·1 per cent. oxide of silver agreeing nearly with the formula $5Ag^2O.C^{24}H^{38}O^5$. (Kawalier, Wien. Akad. Ber. xi. 347.)

KINZIGITE. A name applied by H. Fischer to the mixture of red garnet, mica, and a triclinic felspar (oligoclase), which occurs in veins in primitive gneiss rocks, *e. g.* at Wittichen in the Kinzigthal, Scharzwald, at Auerbach in the Bergstrasse, and other localities, and is regarded by him as an original formation. (Jahrb. Min., 1860, p. 796; 1861, p. 641.)

KIR. A fossil resin, found, with others, on the island of Tschelekän, in the Caspian Sea, and in other neighbouring localities.

KIRWANITE. A hydrated silicate of aluminium, calcium, and iron, occurring in basalt on the Mourne Mountain on the north-east coast of Ireland, in opaque, olive-green radiating fibres, having a specific gravity = 2·941 and hardness = 2. According to an analysis by R. D. Thomson, it contains 40·5 per cent. silica, 23·91 ferrous oxide, 19·78 lime, 11·41 alumina, and 4·35 water (= 99·95), whence Rammelsberg deduces the formula: $2[3(Ca^2O.Fe^2O).2SiO^2].Al^4O^3.2SiO^2.2H^2O$; it is possible, however, that part of the iron may be in the state of ferric oxide.

The mineral blackens and fuses partially before the blow-pipe, and forms a brown glass with soda or borax.

KLAPROTHINE. Syn. with LAZULITE.

KLINOCLASE. Syn. with ABICHITE.

KNEBELITE. A mineral of unknown locality, closely related in composition to olivin, but differing from it considerably in its properties. According to Döbereiner's analysis (Schw. J. xxi. 49), it contains about 32·5 per cent. silica, 32·0 ferrous oxide, and 35·0 manganous oxide, agreeing nearly with the formula $(Mn; Fe)^4SiO^4$, or

$2(Mn^2O\,;\,Fe^2O).SiO^2$.—It is massive, with an uneven and cellular surface, and quite hard. Specific gravity, 3·714. Brittle, with imperfectly conchoïdal fracture. Colour, white to greyish-green, or brown-red and brown. Lustre glistening.

KOBELLITE. A mineral found in the cobalt mine of Hvena in Sweden. It consists, according to Setterberg's analysis (*Berzelius*, *Jahresber*. xx. 215), of 17·86 sulphur, 9·24 antimony, 27·05 bismuth, 40·12 lead, 2·96 iron, 0·80 copper, and 1·45 matrix (=99·48), numbers which may be approximately represented by the formula: $2\left[\begin{matrix}Pb^3\\Sb'''\end{matrix}\right\}S^3\Big]\;.\;3\left[\begin{matrix}Pb^3\\Bi'''\end{matrix}\right\}S^3\Big]$, or $(Pb^{15}\overset{'''}{Sb^2}\overset{'''}{Bi^3})S^{15}$, the lead being partly replaced by iron and copper. It resembles grey antimony, but has a brighter lustre and radiated structure. Specific gravity, 6·29 – 6·32. Soft; of blackish lead-grey to steel-grey colour, with black streak. Dissolves in strong hydrochloric acid, with evolution of sulphydric acid. (Dana, ii. 82; Rammelsberg, *Mineralchemie*, p. 106.)

KOENIGITE. Syn. with BROCHANTITE (i. 664).

KOENLITE. A fossil resin resembling scheererite, found in brown coal at Uznach, at Redwitz in Bavaria, and in the Fichtelgebirge. It contains, according to Schrötter's analysis (Pogg. Ann. lix. 37), 92·43 per cent. C, and 7·71 H, agreeing with the formula nCH. It occurs in soft white crystalline folia and grains, of specific gravity 0·88; melts at 114° (Kraus, Pogg. Ann. xliii. 141), at 107·5° (Trommsdorff, Ann. Ch. Pharm. xxi. 126). Very slightly soluble in cold alcohol, more so in hot alcohol, still more in ether.

KOENLEINITE. A fossil resin from the brown coal of Fassa, in the Eger Valley. It occurs in thin plates, consisting of an aggregate of crystalline scales, perfectly soluble in alcohol and ether, also in strong sulphuric acid; partly soluble in ammonia and in oil of turpentine. (Kenngott, *Mineralogische Untersuchungen*, ii. 111.)

KOETTIGITE. Native arsenate of zinc, $AsZnO^3.4H^2O$, or $Zn^2O.As^2O^5.8H^2O$, containing also nickel and cobalt, with a trace of lime.

As^2O^5	Zn^2O	Co^2O	Ni^2O	H^2O	
37·17	30·52	6·91	2·00	23·40	= 100

according to Naumann, and isomorphous with cobalt-bloom. Massive or in crusts, with crystalline surface and fibrous structure. Cleavage perfect in one direction. Specific gravity = 3·1. Hardness = 2·5 – 3. Lustre of fracture-surface, silky. Colour, light carmine-red and peach-blossom red, of different shades. Streak, reddish-white. Translucent to subtransparent. (Köttig. J. pr. Chem. xlviii. 183; Naumann, *ibid.* 256.—Dana, ii. 418.)

KOKSCHAROWITE. A crystalline mineral occurring with ultramarine, and sometimes intergrown with it. It exhibits two very distinct directions of cleavage, inclined at an angle of 124°. Hardness = 5 to 5·5. It is sometimes colourless, with a strong lustre, sometimes brown and less lustrous. When heated, it becomes darker in colour, and easily melts to a white semitransparent glass (Nordenskiöld Jahresber. 1857, p. 681).—A specimen from the Slüdänka valley, near Lake Baikal, was found by R. Hermann (Jahresber. 1862, p. 726) to contain 45·99 per cent. silica, 18·20 alumina, 2·40 ferrous oxide, 12·78 lime, 16·45 magnesia, 1·06 potash, 1·53 soda, and 0·60 matter lost by ignition (=99·01). Specific gravity = 2·97.

KORITE. See PALAGONITE.

KOUMISS. A vinous liquid, which the Tartars make by fermenting mare's milk. A somewhat similar beverage is prepared in Orkney and Shetland.

KOUPHOLITE. Syn. with PREHNITE.

KRABLITE. Syn. with BAULITE (i. 520).

KRAMERIC ACID. An acid said by Peschier (J. Pharm. vi. 34; x. 348) to exist in rhatany root (*Krameria triandra*). It is crystalline, has a sour and astringent taste, and is not volatile. Its alkaline salts are crystallisable, and their solutions form a white precipitate with lead-salts, yellow with ferric salts. The barium-salt is said not to be decomposed by sulphuric acid or soluble sulphates.

Other chemists who have looked for this acid in rhatany root have not been able to find it.

KRANTZITE. A variety of retinite from the lignite of Latterf, near Bernburg. (See RETINITE).

KRAURITE. Syn. with DUFRENITE.

KREITTONITE. Syn. with SPINEL.

KREMERSITE. Ruby-coloured octahedral chloride of potassium, from Vesuvius. Contains 55·15 per cent. chlorine, 16·89 iron, 12·07 potassium, 0·16 sodium, 15·56 ammonia and water. (Kremers, Pogg. Ann. lxxxiv. 79.)

KRISUVIGITE. Brochantite, from Krisuvig in Iceland.

KROKOÏTE. Syn. with CROCOÏSITE (ii. 109.)

KUPRAPHITE. Syn. with TYROLITE.

KYAMETHINE. Syn. with CYAMETHINE (ii. 188).

KYANETHINE. Syn. with CYANETHINE (ii. 189).

KYANITE or *Cyanite.* A silicate of aluminium, $Al^4O^3.SiO^2$, occurring in triclinic prisms, $oP . \infty\bar{P}\infty . \infty\breve{P}\infty . \infty{,}P . \infty P'{,} . 2\breve{P}\infty$. Crystals usually bladed. Angles $oP : \infty\breve{P}\infty = 93° 15'$; $\infty P : \infty\bar{P}\infty = 100° 50'$; $oP : \infty{,}P = 98° 58'$; $oP : \infty P'{,} = 96° 42'$; $\infty\bar{P}\infty : \infty\breve{P}\infty = 106° 16'$; $\infty{,}P : \infty P'{,} = 97° 4'$; $\infty\bar{P}\infty : \infty{,}P = 145° 41'$; $\infty\breve{P}\infty : \infty P'{,} = 131° 23'$; $\infty\breve{P}\infty : 2\breve{P}\infty = 159° 15'$. Cleavage perfect parallel to the smoother lateral plane; imperfect parallel to the base. Twins, of two kinds, with face of composition $\infty\bar{P}\infty$, and planes $\infty\breve{P}\infty$, meeting at an angle; in one kind the planes oP are coincident, in the other they form a re-entering angle. Also coarse-bladed, columnar; also fibrous. Hardness = 6 to 7·25. Specific gravity = 3·559; of white kyanite 3·675; of blue transparent kyanite from the Tyrol, 3·661 (Erdmann). Lustre vitreous to pearly. Colour generally pale blue, often deeper along the middle of the prisms; sometimes white or blue, with white margins; also grey, green, and black. Streak uncoloured. Translucent and sometimes transparent. The crystals may often be easily scratched on the lateral surface, while they are very hard at the extremities.

Kyanite remains unaltered when simply heated before the blowpipe; melts to a transparent, colourless glass with borax, and gives a deep blue colour with cobalt-solution.

Pure kyanite would contain 37·5 per cent. silica, and 62·5 alumina. The following analyses show that it does not deviate much from this composition:

	Arfvedson.		Smith and Brush.	Marignac.	Erdmann.	Smith and Brush.
	Rörass.	St. Gothard.	New York.	St. Gothard.	Rörass.	New York.
Silica . .	36·4	36·9	37·03	36·60	34·40	37·20
Alumina . .	63·8	64·7	61·90	62·66	61·86	59·02
Ferric oxide .	. .	. .		0·84	0·52	2·08
Cupric oxide .	. .	. .	. .	. .	0·19	
Water . .	. .	. .	0·85	. .	. .	1·03
	100·2	101·6	99 78	100·10	96·97	99·33

Kyanite occurs principally in gneiss and mica-slate. Transparent crystals are found at St. Gothard, in Switzerland; at Greiner and Pfitsch, in the Tyrol: also in Styria, Carinthia, and Bohemia; at Pontivy, in France; and at Villa Rica, in South America. It occurs also in many localities in the United States: the specimens analysed by Smith and Brush were from Monro County, New York.

Bamlite (i. 499), from Bamle, in Norway, and xenolite (*q. v.*), have nearly the same composition as kyanite. Woerthite, from near St. Petersburg, containing 40·6 per cent. SiO^2, 53·50 Al^4O^3, 1·00 Mg^2O and 4·63 water, and Thomson's hydrobucholzite (probably from Sardinia), which contains 41·35 SiO^2, 49·53 Al^4O^3, 4·85 water and 3·12 gypsum, are probably hydrous kyanites. Kyanite has also been observed altered to talc and steatite. (Dana, ii. 265.)

KYANOL. Syn. with PHENYLAMINE.

KYMATIN. Syn. with HORNBLENDE.

KYAPHENINE or **CYAPHENINE.** $(C^{21}H^{15})'''N^3$.—A compound polymeric with cyanide of phenyl (benzonitrile), C^7H^5N, obtained by heating pulverised cyanate of potassium with chloride of benzoyl:

$$3C^7H^5OCl + 3CNKO = C^{21}H^{15}N^3 + 3KCl + 3CO^2.$$

It is a hard neutral substance, exhibiting a crystalline fracture; melts at 224°, and distils without alteration at or a little above 350°; is soluble in water, slightly soluble in alcohol and ether. When heated with caustic potash, it decomposes, with copious evolution of ammonia. Sulphuric acid dissolves it, forming an acid whose barium-salt is soluble in water. Strong hydrochloric acid does not dissolve it, even at the boiling heat. Nitric acid of ordinary strength is also without action upon it; but fuming nitric acid dissolves it, with great rise of temperature, but without evolution of gas; and by evaporating the solution or mixing it with water, nearly the whole of the cyaphenine is precipitated in the form of a nitro-compound, $C^{21}H^{12}(NO^2)^3N^3$, which crystallises in needles.

KYMATIN. Syn. with HORNBLENDE.

KYNURENIC ACID. (Liebig, Ann. Ch. Pharm. lxxxvi. 125; cviii. 354.)—An acid sometimes deposited from the urine of dogs. From the urine of a dog which had been fed on fat alone, or on fat mixed with a small portion of meat, Liebig obtained it by evaporating, adding hydrochloric acid and leaving the liquid to stand for some time; the urine of dogs fed exclusively on lean meat yielded only traces. The deposit dissolves in lime-water, and on diluting the solution with water, and adding hydrochloric acid, kynurenic acid is deposited in very slender, colourless needles; from concentrated solutions, as a powder.

Kynurenic acid reddens litmus; when heated in a glass tube, it melts to a brown liquid, which then sublimes completely, forming a white silky crystalline sublimate, and leaving a trace of charcoal. The precipitated acid is insoluble in alcohol and in ether; the sublimed acid dissolves in alcohol. It dissolves easily in boiling hydrochloric acid (whereby it is distinguished from uric acid), and in dilute sulphuric and nitric acids (in the latter without perceptible alteration, even on boiling). Cold concentrated sulphuric acid dissolves it without alteration; but on heating the solution, it turns brown, and, on addition of water, deposits a lemon-yellow, amorphous precipitate, often mixed with crystals of the unaltered acid.

Kynurenic acid is a very weak acid. It dissolves easily in caustic alkalis, and, with aid of heat, in alkaline carbonates, lime-water and baryta-water, neutralising the bases and forming crystallisable salts. The *barium-salt* forms plumose groups of nacreous needles; the *calcium-salt*, stellate groups of short hard needles. Both salts are sparingly soluble in water.

The acid is precipitated from the solution of the barium-salt by carbonic acid. It gave by analysis 61·6 to 61·9 per cent. carbon, 4·7 to 4·4 hydrogen, and 8·7 to 9·4 nitrogen. When heated alone or with lime, it yields a volatile oil, having the odour of benzonitrile.

KYPHOLITE. Syn. with SERPENTINE.

KYROSITE. White iron pyrites from the mine Briccius, near Annaberg.

L.

LABDANUM or **LADANUM.** A resin which exudes in drops from the leaves and branches of the *Cistus creticus* and *C. cypricus*, shrubs growing in Greece and Turkey. It is generally black, solid, tenacious, and somewhat moist; softens between the fingers, and exhales an odour like that of ambergris. A sample analysed by Guibourt (*Histoire des Drogues*, iii. 601) contained 86 per cent. resin and volatile oil, 7 wax, 1 aqueous extract, and 6 earthy matter and hairs. Commercial labdanum is often largely adulterated with black sand. According to Johnston, labdanum-resin contains 73·2 per cent. carbon and 10·0 hydrogen; a composition which may be approximately represented by the formula $C^{20}H^{30}O^{3}$ (calc. 75·5 C, 9·4 H, and 15·1 O).

Labdanum in sticks is prepared in Portugal, Spain, and the South of France, by boiling the leaves and branches of *Cistus ladaniferus*.

LABRADORITE. *Labrador Felspar. Anhydrous Scolecite. Mauilite. Silicite. Scolexerose.*—A mineral species belonging to the felspar group, and represented by the formula $M^2O.Al^4O^3.3SiO^2$, or $\left.\begin{matrix}(Si^3)^{xii}\\(Al^4)^{vi}\\M^2\end{matrix}\right\}O^{10}$, where M denotes calcium and sodium, and occasionally also magnesium and potassium.

Labradorite occurs in triclinic crystals, in which $oP : \infty\breve{P}\infty = 86° 32'$; $oP : \infty{}'P = 114° 48'$; $\infty\breve{P}\infty : \infty P'_{,} = 119° 16'$. It forms twins like those of albite (ii. 621). Cleavage perfect parallel to oP; distinct parallel to $\infty\breve{P}\infty$, in which direction also the faces are usually striated; indistinct parallel to $\infty P'_{,}$. Also massive, with distinct cleavage. Hardness = 6. Specific gravity = 2·67 to 2·76. Lustre of oP pearly, passing into vitreous; elsewhere vitreous or subresinous. Colour usually grey, of various shades; also greenish, reddish, or yellowish. Some varieties, especially that from Labrador, exhibit a beautiful play of colours when viewed in certain directions: this effect is best seen in cut and polished specimens. Streak uncoloured. Fracture glistening. Translucent in a low degree. Less easily frangible than common felspar.

Before the blowpipe on charcoal it fuses, with less difficulty than orthoclase, to a colourless glass. With oxide of nickel and borax it forms a blue bead. When pulverised, it is entirely dissolved by hydrochloric acid, which does not attack either orthoclase or albite.

Analyses: *a.* From Campsie in Scotland, where it occurs in porphyritic greenstone (Lehunt, Ed. N. Phil. J. 1832, p. 86). *b.* From Etna, where it occurs as a constituent of lava (v. Waltershausen, *Vulcanishe Gesteine*, 1853, p. 24). *c.* From Faroë, (Forchhammer, J. pr. Chem. xxx. 385). *d.* From Labrador (v. Waltershausen *loc. cit.*). *e.* From Egersund, in Norway; violet-grey with brilliant play of colours (Kersten, Pogg. Ann. lxiii. 123). *f.* From the hypersthene-rock of Neurode, in Silesia; bluish-grey (v. Rath, Pogg. Ann. xcv. 538). *g.* From the gabbro of the same locality; bluish-white (v. Rath, *ibid.*). *h.* From the melaphyre between Botzen and Collman, in the Tyrol; light greyish green. (Delesse, J. pr. Chem. xliii. 447; xlv. 219). *i.* From the trachydolerite of Guadaloupe (Deville, *Rammelsberg's Mineralchemie*, p. 598). *k.* *Scolexerose*, from Pargas, Finland (Nordenskiöld, Schw. J. xxxi. 417). *l.* *Silicite*, from Antrim, Ireland. (Thomson, Phil. Mag. 1843, p. 417.)

	SiO^2.	Al^4O^3.	Fe^4O^3.	Ca^2O.	Mg^2O.	Na^2O.	K^2O.	H^2O.	
a.	54·67	27·89	0·31	10·60	0·18	5·05	0·49	. .	= 99·19
b.	53·56	25·82	3·41	11·68	0·52	4·00	0·54	0·95	=100·48
c.	52·52	30·03	1·72	12·58	0·19	4·51	. .	. .	=101·55
d.	53·75	27·06	0·99	9·58	0·47	1·25	7·53	0·62	=101·25
e.	52·20	29·05	0·80	12·10	0·13	4·70		. .	= 98·98
f.	52·55	28·32	2·44	11·61	0·48	4·52	0·64	0·62	=101·18
g.	50·31	27·31	1·71	10·57	0·78	4·81	1·55	2·20	= 99·24
h.	53·23	27·73	1·50	8·28	0·93	7·38		0·95	=100·00
i.	54·25	29·89	. .	11·12	0·70	3·63	0·33	. .	= 99·92
k.	54·13	29·23	. .	15·45	. .	. .	. .	1·07	= 99·88
l.	54·8	28·4	Fe^2O 4 0	12·4	. .	. .	. .	0·6	=100·2

If the number of molecules of lime be supposed to be three times as great as that of the soda, the above formula, which then becomes $\left.\begin{matrix}\tfrac{3}{4}Ca\\ \tfrac{1}{4}Na\end{matrix}\right\}O.Al^4O^3.3SiO^2$, gives 53·1 per cent. SiO^2, 30·1 Al^4O^3, 12·3 Ca^2O, and 4·5 Na^2O.

Labradorite is more subject to alteration than other felspars; perhaps because it contains both potash and soda. Partial decomposition is shown, either by the diminished quantity of these bases, or by the consequently increased proportion of silica. The best examples of unaltered labradorite in the preceding table are perhaps *e, f, g, h,* and *i*; *k* and *l*, if the analyses are correct, afford decided indications of decomposition. For numerous analyses of labradorite, and of felspars allied to it, see *Rammelsberg's Mineralchemie*, pp. 597—603.

Labradorite is a constituent of some lavas, as those of Etna and Vesuvius; of many porphyries, as the oriental *verd antique* of Greece; of dolerite; of certain hornblende-rocks, granites, and syenites; of some porphyritic greenstones, as at Campsie in Scotland; of melaphyres, as in the Tyrol. On the coast of Labrador, whence it was originally brought, it is associated with hornblende, hypersthene, and magnetic iron ore. (Dana, ii. 238.)

LABURNIC ACID. An acid said to be contained, together with cytisine (ii. 311) and two neutral bitter principles, in the seeds, bark, and other parts of *Cytisus Laburnum.* (T. Scott Gray, Arch. Pharm. [3] xlii. 160.)

LAC is a substance well known in Europe under the different appellations of stick-lac, shell-lac, and seed-lac. The first is the lac in its natural state, encrusting small branches or twigs. Seed-lac is the stick-lac separated from the twigs, appearing in a granulated form, and probably deprived of part of its colouring matter by boiling. Shell-lac is the substance which has undergone a simple purification, as mentioned below. Beside these we sometimes meet with a fourth, called lump-lac, which is the seed-lac melted and formed into cakes.

Lac is the product of the *Coccus lacca*, which deposits its eggs on the branches of a tree called Bihar, in Assam, and other parts of India. It appears designed to answer the purpose of defending the eggs from injury, and affording food for the maggot in a more advanced state. It is formed into cells, finished with as much art and regularity as a honeycomb, but differently arranged; and the inhabitants collect it twice a year, in the months of February and August. For purification, it is broken into small pieces, and put into a canvas bag of about four feet long, and not above six inches in circumference. Two of these bags are in constant use, each of them being held by two men. The bag is placed over a fire, and frequently turned, till the lac is liquid enough to pass through its pores; then taken off the fire, twisted in different directions, and a the same time dragged along the convex part of a plantain tree prepared for this purpose; and while this is being done, the other bag is being heated, to be afterwards treated in the same way. The mucilaginous and smooth surface of the plantain tree prevents it from adhering; and the degree of pressure regulates the thickness of the coating of lac, at the same time that the fineness of the bag determines its clearness and transparency.

Stick-lac contains in 100 parts, resin 68, colouring extract 10, wax 6, gluten 5·5, extraneous substances 6·5; seed-lac contains resin 88·5, colouring extract 2·5, wax 4·5, gluten 2; shell-lac contains resin 90·9, colouring extract 0·5, wax 4, nitrogenous matter 2·8. (Hatchett.)

In India, lac is fashioned into rings, beads, and other trinkets; sealing-wax, varnishes, and lakes for painters, are made from it; it is much used as a red dye, and the resinous part, melted and mixed with about thrice its weight of finely-powdered sand, forms polishing stones. Lapidaries mix powder of corundum with it in a similar manner.

The colouring matter is soluble in water; but 1 pt. of borax to 5 of lac renders the whole soluble by digestion in water, nearly at a boiling heat. This solution is equal, for many purposes, to spirit varnish, and is an excellent vehicle for water-colours, as, when once dried, water has no effect upon it. Aqueous potash, soda, and carbonate of soda, likewise dissolve it; so does nitric acid, if digested with it in sufficient quantity for 48 hours.

The colouring matter of lac loses much of its beauty by keeping; but when freshly extracted, and precipitated as a lake, it is less liable to injury. Mr. Stephens, a surgeon in Bengal, sent home a large quantity precipitated in this way with alum; it afforded a good scarlet to cloth previously yellowed with quercitron.

Lac is the basis of the best sealing-wax. A good composition for red sealing-wax is 48 pts. of shellac, 12 oil of turpentine, 1 Peru balsam, and 36 vermillion. U.

LAC-DYE. A product obtained from lac, and used for producing a red dye, especially on wool. To obtain it, stick-lac freed from remains of stalks is pulverised and exhausted with warm water; and the colouring matter left on evaporating the solution is made into square cakes, and sent into the market as lac-dye. The residue yields seed-lac (*Lac in granis*), which is worked up into shell-lac. The proximate constitution of lac-dye is not exactly known; it contains, however, a considerable quantity of resin, and a red colouring matter, derived from the insects (*Coccus laccæ*), which may be partly extracted by water, more completely by acids, especially sulphuric or hydrochloric acid. The following processes are adopted for rendering the dye fit for use:

1. A mixture of 4 pts. lac with strong sulphuric acid is allowed to stand for 24 hours in summer and 48 in winter; then diluted and stirred with 3½ pts. of water, and again left to clarify. The clear liquid is poured into an iron pot, and mixed with the wash-water of the previous residue; the solution is mixed with a quantity of lime sufficient to neutralise ⅔ of the sulphuric acid, and the precipitate of gypsum is removed: the liquid is then ready for use. This is the mode of preparation chiefly adopted in this country.

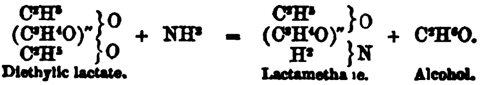
2. Thirty-two pts. of lac-dye are triturated with 10 to 12 pts. of sulphuric acid of specific gravity 1·85, or hydrochloric acid of specific gravity 1·13, each diluted with three times its weight of water. The mixture is left to itself for 48 hours in winter, or 24 in summer, and then mixed with the requisite quantity of river-water.

3. Thirty-two pts. of lac-dye are triturated with 12 pts. of hydrochloric acid of specific gravity 1·148, diluted with an equal weight of water; the mixture is left for 24 hours and frequently stirred, and then diluted with water.

To dye with the colour thus prepared, each pound is mixed with three-quarters of a pint of so-called lac-spirit, a solution of stannous chloride prepared by dissolving one pound of tin in 20 pounds of fuming hydrochloric acid, the mixture being left to itself for six hours before use. (Handw. d. Chem. iv. 748. See also *Ure's Dictionary of Arts, &c.* ii. 626.)

LACTAMETHANE. *Ethyl-lactamide*, $C^5H^{11}NO^2 = \left.\begin{matrix} C^2H^5 \\ (C^3H^4O)'' \\ H^2 \end{matrix}\right\} \begin{matrix} O \\ \\ N \end{matrix}$. (Wurtz, Ann. Ch. Phys. [3] lix. 175.)—This compound is formed when diethylic lactate is treated with aqueous ammonia, and the mixture is left to stand for one or two days; or when an alcoholic solution of the ether is saturated with ammonia and heated in a close vessel. The former process is, according to Wurtz, to be preferred. After expelling the excess of ammonia and water by evaporation in the water-bath, the lactamethane remains as a liquid, which solidifies on cooling to a beautiful crystalline mass, formed of broad, brilliant plates, slightly greasy to the touch. These crystals are soluble in water, alcohol, and ether; they melt at 62° or 63° to a colourless liquid, and boil at 219° under a barometric pressure of 761 mm., distilling without alteration.

The formation of lactamethane may be represented by the equation



$$\left.\begin{matrix} C^2H^5 \\ (C^3H^4O)'' \\ C^2H^5 \end{matrix}\right\} \begin{matrix} O \\ \\ O \end{matrix} + NH^3 = \left.\begin{matrix} C^2H^5 \\ (C^3H^4O)'' \\ H^2 \end{matrix}\right\} \begin{matrix} O \\ \\ N \end{matrix} + C^2H^6O.$$

Diethylic lactate. Lactamethane. Alcohol.

By ebullition with potash, it is decomposed into ammonia and ethyl-lactate of potassium:

$$\underset{\text{Lactamethane.}}{\begin{matrix}C^2H^5\\(C^3H^4O)''\\H^2\end{matrix}\begin{matrix}\}O\\ \\ \}N\end{matrix}} + KHO = \underset{\text{Ethyl-lactate of potassium.}}{\begin{matrix}C^2H^5\\(C^3H^4O)''\\K\end{matrix}\begin{matrix}\}O\\ \\ \}O\end{matrix}} + NH^3.$$

G. C. F.

LACTAMIC ACID. Syn. with ALANINE (i. 63). It is also produced by the action of very strong solution of ammonia on chloropropionate of ethyl at 100°. (Kolbe, Ann. Ch. Pharm. cxiii. 220.)

Lactamate of ammonium (so called), $C^6H^{14}N^2O^4 = \begin{matrix}H^2\\(C^3H^4O)''\\(C^3H^4O)''\\H^4N\end{matrix}\begin{matrix}\}N\\ \}O\\ \\ \}O\end{matrix}$.—Formed by the action of ammonia-gas on lactic anhydride (DILACTIC ACID, p. 461) (Pelouze); or by saturating a solution of lactic anhydride in absolute alcohol with dry ammonia, and evaporating the solution. Tabular crystals, very easily soluble in water and alcohol. On adding dichloride of platinum to the solution, freed by boiling from excess of ammonia, only part of the nitrogen is precipitated as chloroplatinate of ammonium; but after boiling the filtrate for an hour, it gives a further precipitate with dichloride of platinum—a proof that part only of the nitrogen exists in the form of ammonium-salt. (Laurent, Compt. chim. 1845, p. 151.) G. C. F.

LACTAMIDE. $C^3H^7NO^2 = \begin{matrix}H\\(C^3H^4O)''\\H^2\end{matrix}\begin{matrix}\}O\\ \\ \}N\end{matrix}$. (Isomeric with alanine or lactamic acid (i. 63), $C^3H^7NO^2 = \begin{matrix}H^2\\(C^3H^4O)''\\H\end{matrix}\begin{matrix}\}N\\ \\ \}O\end{matrix}$.)—Obtained—1. By the action of ammonia gas on lactide (Pelouze; Wurtz and Friedel, Ann. Ch. Phys. [3] lxiii. 108).—2. By the action of an alcoholic solution of ammonia on lactide (Wurtz and Friedel, *loc. cit.*).—3. By saturating monethylic lactate with ammonia and leaving the liquid to stand. (Brüning, Ann. Ch. Pharm. civ. 197.)

It forms small prisms, which dissolve easily in *water* and *alcohol*, but do not combine either with acids or bases. It is decomposed, by boiling with alkalis or acids, into ammonia and lactic acid.

The above formula represents lactamide as derived from the double molecule $\left.\begin{matrix}H^2O\\H^3N\end{matrix}\right\}$ by the substitution of the radicle C^3H^4O for H^2. The substances described under the names lactamethane (p. 452), and lactethylamide (*vid. inf.*), are ethylised derivatives of lactamide; the former by the substitution of C^2H^5 for the hydrogen-atom of the water-residue contained in lactamide, the latter by the substitution of C^2H^5 for one of the hydrogen atoms of the ammonia-residue. These relations are expressed in the rational formulæ by which lactamethane, lactethylamide, and lactamide are respectively represented at the places referred to. G. C. F.

LACTETHYLAMIDE. $C^5H^{11}NO^2 = \begin{matrix}H\\(C^3H^4O)''\\C^2H^5.H\end{matrix}\begin{matrix}\}O\\ \\ \}N\end{matrix}$. Isomeric with lactamethane (Wurtz and Friedel, Ann. Ch. Phys. [3] lxiii. 110). Formed by the action of ethylamine on lactide. When these two substances are brought together, the ethylamine immediately begins to boil. If the operation is performed in a close vessel, and with anhydrous materials, the whole solidifies to a crystalline mass. This product, when purified by one crystallisation from alcohol, melts at 48°, and may be cooled to 40° without freezing; but as soon as crystallisation has commenced, the thermometer rises to 46·5°. Lactethylamide distils without alteration at 260°. Its formation is represented by the equation

$$\underset{\text{Lactide.}}{C^3H^4O^2} + \underset{\text{Ethylamine.}}{C^2H^7N} = \underset{\text{Lactethylamide.}}{C^5H^{11}NO^2}.$$

Alkalis decompose it into ethylamine and alkaline lactate.

$$\underset{\text{Lactethylamide.}}{\begin{matrix}H\\(C^3H^4O)''\\C^2H^5.H\end{matrix}\begin{matrix}\}O\\ \\ \}N\end{matrix}} + KHO = \underset{\text{Lactate of potassium.}}{\begin{matrix}H\\(C^3H^4O)''\\K\end{matrix}\begin{matrix}\}O\\ \\ \}O\end{matrix}} + \underset{\text{Ethylamine.}}{C^2H^5.H^2N.}$$

G. C. F.

LACTIC ACID. *Milchsäure*, $C^3H^6O^3 = \left.\begin{matrix}(C^3H^4O)''\\H^2\end{matrix}\right\}O^2$. (Gm. xi. 472).—This acid was discovered by Scheele in sour milk, and first recognised as a peculiar acid by Berzelius. Braconnot found in the wash-liquor of the preparation of wheat-starch, in the fermented juice of mangold-wurzel, and other fermented vegetable extracts, an acid which he designated *nanceic acid*, but which was afterwards shown to be identical with the acid of sour milk. Berzelius demonstrated the presence of the same or an isomeric acid in the juice of the flesh of animals recently killed—a result which was confirmed by Liebig in his classical investigation of flesh-juice (see SARCOLACTIC ACID, p. 457). More recently, the chemical relations of lactic acid have been investigated by Strecker (Ann. Ch. Pharm. lxxxi. 247; xci. 352), Wurtz (Ann. Ch. Phys. [3] lix. 161), Wurtz and Friedel (*ibid.* lxiii. 101), and Kolbe (Chem. Soc. Qu. J. xii. 15); and the lactates have been chiefly studied by Pelouze (Ann. Ch. Phys. [3] xiii. 257), and by Engelhardt and Maddrell (Ann. Ch. Pharm. lxii. 83; lxx. 241).

Formation.—1. By a peculiar fermentation, the *lactic acid fermentation*, of various kinds of sugar, and of dextrin: this fermentation precedes the butyric acid fermentation. As all the substances of the sugar tribe have the same proportional composition as lactic acid, with a few atoms of water more or less, the transformation is easily explained: thus, with milk-sugar:

$$\underset{\text{Milk-sugar.}}{C^{12}H^{20}O^{10}} \quad + \quad 2H^2O \quad = \quad \underset{\text{Lactic acid.}}{4C^3H^6O^3}$$

The lactic fermentation requires a temperature between 20° and 40° C., and the presence of water and of certain ferments, viz., albuminoïdal substances in a peculiar state of decomposition, such as casein, gluten, or animal membranes, particularly the coating of the stomach of the calf (rennet), or dog, and bladder.

2. Tritylglycol, in presence of platinum-black, is converted into lactic acid by the oxygen of the air (Wurtz):

$$\underset{\text{Tritylglycol.}}{C^3H^8O^2} \quad + \quad O^2 \quad = \quad \underset{\text{Lactic acid.}}{C^3H^6O^3} \quad + \quad H^2O$$

3. Chloropropionic acid yields chloride of silver and lactic acid, when it is heated with water and oxide of silver. (Wurtz, Ann. Ch. Phys. [3] lix. 165):

$$\underset{\substack{\text{Chloropropionate of}\\ \text{silver.}}}{C^3H^4ClAgO^2} \quad + \quad H^2O \quad = \quad \underset{\text{Lactic acid.}}{C^3H^6O^3} \quad + \quad AgCl$$

Similarly, bromopropionic acid yields lactic acid and bromide of silver, when treated with oxide of silver in presence of water (Friedel and Machuca, Ann. Ch. Pharm. cxx. 286). Iodopropionic acid (formed by the action of iodide of phosphorus on glyceric acid) appears to yield a peculiar modification of lactic acid when treated as above. (Beilstein, *ibid.* p. 234.)

4. By the action of nitrous acid upon alanine; as when the vapours evolved from a mixture of starch and nitric acid, after being passed through a cold vessel which stops any undecomposed nitric acid, are conducted into aqueous alanine; the action is attended with copious evolution of nitrogen:

$$\underset{\text{Alanine.}}{C^3H^7NO^2} \quad + \quad \underset{\text{Nitrous acid.}}{NO^2H} \quad = \quad \underset{\text{Lactic acid.}}{C^3H^6O^3} \quad + \quad H^2O \quad + \quad N^2$$

5. Pyruvic (pyroracemic) acid, treated in aqueous solution with sodium-amalgam (Wislicenus, Ann. Ch. Pharm. cxxvi. 227), or with zinc in presence of dilute acetic acid (Debus, Chem. Soc. J. xvi. 260), is converted into a salt of lactic acid:

$$\underset{\text{Pyruvic acid.}}{C^3H^4O^3} \quad + \quad H^2 \quad = \quad \underset{\text{Lactic acid.}}{C^3H^6O^3}$$

6. When hydroxycyanide of ethylene, $\left.\begin{matrix}(C^2H^4)''\\ H\end{matrix}\right\}\begin{matrix}CN\\ O\end{matrix}$ (obtained from hydroxychloride of ethylene by double decomposition with cyanide of potassium), is boiled with aqueous alkalis, it is resolved into ammonia and (sarco-) lactic acid. (Wislicenus, Ann. Ch. Pharm. cxxviii. 6):

$$\underset{\substack{\text{Hydroxycyanide}\\ \text{of ethylene.}}}{C^3H^5NO} \quad + \quad 2H^2O \quad = \quad \underset{\text{Lactic acid.}}{C^3H^6O^3} \quad + \quad H^3N$$

Ethyloxycyanide of ethylidene, $\left.\begin{matrix}(C^2H^4)''\\ C^2H^5\end{matrix}\right\}\begin{matrix}CN\\ O\end{matrix}$ (obtained by digesting ethyloxychloride of ethylidene [ii. 600] with cyanide of potassium in a sealed tube), yields ordinary lactic acid, and a small quantity of ethyl-lactic acid, when similarly treated. (Wislicenus, *op. cit.* p. 14.)

7. Oxychloride of carbon combines directly with ethylene, forming chloride of lactyl:

$$COCl^2 + C^2H^4 = C^3H^4OCl^2,$$

whence lactic acid can be obtained by well-known processes. (Lippmann, Ann. Ch. Pharm. cxxix. 81; Ann. Ch. Phys. [4] i. 485.)

Preparation.—a. *From various kinds of Sugar.*—1. An aqueous solution of 100 pts. of grape-sugar (cane- or milk-sugar), exhibiting the density of 8° to 10° Bm., is mixed with 8 or 10 pts. of fresh sour cheese, as purchased in the market, or 100 pts. of sugar are dissolved in 100 to 150 pts. of milk, and such a quantity of water that the liquid exhibits a density of 10° Bm.; and either of these mixtures is placed, together with 50 pts. of chalk, in an open vessel, and exposed to the sun for several weeks, with frequent agitation, till the resulting lactate of calcium begins to change into butyrate (Pelouze and Gelis). As lactate of calcium is much less soluble than butyrate, the conversion of the former into the latter may be recognised, when strong solutions of sugar are used, by the diminution of the crystalline mass produced at first. If the process be too soon interrupted, a large quantity of sugar remains unaltered.

2. Six pounds of cane-sugar and half an ounce of tartaric acid (which serves to convert the cane-sugar into glucose) are dissolved in 26 pounds of boiling water; 3 pounds of levigated chalk added after two days, together with 4 ounces of stinking hand-cheese, suspended in 8 pounds of sour milk (decaying cheese favours the production of lactic acid and retards its conversion into butyric acid); the mixture set aside at a temperature between 30° and 35°, and well stirred every day till, in the course of six or eight days, it is converted into a stiff paste of lactate of calcium; this paste is boiled for an hour with half an ounce of quicklime and 20 pounds of water; the solution strained through a cloth filter and evaporated to a syrup; the crystalline mass which forms in four days, pressed, first by itself, then three or four times, after having been each time stirred up, with $\frac{1}{10}$ pt. of cold water; and the lactate of calcium thus purified is dissolved in twice its weight of boiling water. To the solution of every 32 pts. of the calcium-salt there is then added a mixture of 7 pts. oil of vitriol and 7 pts. water; the lactic acid, while still hot, is strained through linen to separate it from sulphate of lime; the filtrate obtained from 7 pts. of oil of vitriol is boiled with 1$\frac{5}{8}$ pts. carbonate of zinc for a quarter of an hour (by longer boiling a very sparingly soluble basic salt is formed); the liquid is filtered boiling hot; the colourless crystalline grains of lactate of zinc which separate on cooling, are freed from sulphuric acid by washing with cold water; and additional quantities of crystalline grains are obtained by evaporating the mother-liquor, almost to the end. Lastly, 1 pt. of the zinc-salt is dissolved in 7$\frac{1}{2}$ pts. of boiling water; sulphuretted hydrogen passed through the solution as long as sulphide of zinc is precipitated; and the filtrate boiled and evaporated on the water-bath to a syrup, whereupon 8 pts. of the zinc-salt yield 5 pts. of syrupy lactic acid (Bensch, Ann. Ch. Pharm. lxi. 174). By this process, 100 pts. of cane-sugar yield 117 pts. of lactate of calcium, which, if the sugar was white, is colourless, and does not require to be purified by pressure. If the carbonate of zinc contains lime and magnesia, these bases pass over to the lactic acid, which, after being evaporated to a syrup, must be dissolved in ether, and separated from the lactates of calcium and magnesium by filtration and evaporation. The calcium-salt may, however, without first preparing the zinc-salt from it, be freed by repeated crystallisation from a nitrogenous substance which obstinately adheres to it; its solution in the smallest possible quantity of water, mixed with a quantity of pure sulphuric acid not quite sufficient to decompose it; the mixture heated with alcohol till the sulphate of calcium is completely separated; the filtrate evaporated to a syrup; the syrup dissolved in ether; and the ethereal solution filtered and evaporated. (Engelhardt and Maddrell.)

Lautemann (Ann. Ch. Pharm. cxiii. 242) recommends the following modification of Bensch's process of preparation:—Retaining the proportions of sugar, tartaric acid, milk, and cheese indicated by the latter, he takes one-third more water, uses 1,200 grms. oxide of zinc (commercial zinc-white) instead of levigated chalk, and keeps the temperature as constantly as possible between 40° and 45° during the fermentation. After eight or ten days, the inside of the vessel is lined with white crystals of lactate of zinc, which can be obtained pure by one or two crystallisations from boiling water. The lactic acid prepared from the zinc-salt generally contains mannite, which does not completely crystallise out from the concentrated acid. To separate this, the aqueous acid is shaken up with ether, and then the ethereal layer is pipetted off and evaporated: it then leaves pure lactic acid.

3. The solution of 300 grms. of milk-sugar in 4 litres of milk is placed in the open air at a temperature of 25° to 30°, and neutralised with acid carbonate of sodium as often as it becomes sour, perhaps every two days; boiled when it no longer turns acid; filtered from the curd; carefully evaporated to a syrup; and the syrup dissolved in moderately warm alcohol of 38° Bm. By treating this filtered alcoholic solution of lactate of sodium with sulphuric acid to precipitate the sodium, and saturating the filtered lactic acid with chalk, crystallised lactate of calcium is obtained, and may be purified by further treatment. (Boutron and Frémy, J. Pharm. xxvii. 341.)

b. *From milk which has turned sour.*—1. Scheele evaporates sour whey to $\frac{1}{8}$; filters the liquid from the curd; precipitates the phosphoric acid from it with lime; filters; dilutes with 3 pts. water; precipitates the lime by careful addition of oxalic acid; filters; evaporates to the consistence of honey; extracts the lactic acid with alcohol;

filters; dilutes with water, and evaporates. Berzelius digests the acid thus obtained with carbonate of lead; filters; precipitates the dissolved lead with sulphydric acid, filters, and evaporates.—2. The filtered solution of sour whey evaporated nearly to dryness, in strong alcohol, is mixed with alcoholic tartaric acid, as long as any precipitate of tartrate of potassium, sodium, and calcium is formed; the liquid decanted after 24 hours, and evaporated; the residue dissolved in water; the solution digested with carbonate of lead, till lead dissolves in it; the filtrate evaporated, neutralised with carbonate of barium, again filtered, and diluted with water; the whole of the barium precipitated with sulphate of zinc; and the filtrate evaporated till lactate of zinc crystallises out (Berzelius, Lehrb. Ausg. 5, v. 241. For the earlier methods of Berzelius, see Pogg. Ann. xix. 26). W. Engelhardt (Zeitschr. Chem. Pharm. 1861, p. 643) gives the following process for the preparation of lactate of zinc, from which he then obtains lactic acid by decomposing the hot solution of the zinc-salt with sulphydric acid, filtering and evaporating. Sour whey, to which $\frac{1}{20}$ of its weight of powdered milk-sugar has been added, is exposed to the proper temperature for the lactous fermentation, and every one or two days the free acid is neutralised with crushed carbonate of sodium taken from a previously weighed quantity. When at last the acid reaction does not reappear after two or three days, the liquid is heated to boiling, and sulphuric acid is added, drop by drop, so as to produce a distinct acid reaction. A quantity of sulphate of zinc equal in weight to the carbonate of sodium used is then dissolved in twice its own weight of water, and mixed with the other boiling liquid; the cheesy portions which immediately separate at the surface are removed by filtration through flannel-bag and the clear liquid is set aside to crystallise. After a day or two, the crystalline deposit of lactate of zinc may be removed and washed with cold water. The quantity remaining in the mother-liquor is insignificant. (For Cap and O. Henry's process, see J. Pharm. xxv. 138; also Ann. Ch. Pharm. xxx. 106.)

Properties.—Lactic acid is a colourless liquid of syrupy consistence, and specific gravity 1·215 at 20·5° C. It is inodorous, but has an intensely sour taste. It absorbs moisture from the air; dissolves in all proportions in water and alcohol, somewhat less freely in ether. It does not solidify at −24° C.

Decompositions.—1. *Dry distillation.* The acid, when very gradually heated, becomes less viscid; gives off at 130°, slowly and without evolution of gas, colourless water, together with a small quantity of lactic acid, and leaves a pale yellow, solid, easily fusible, extremely bitter residue of *lactic anhydride* (dilactic acid), $C^6H^{10}O^5 = 2C^3H^6O^3 - H^2O$. This residue remains unaltered up to 250°, but from 250° to 300°, at which temperature the decomposition is complete, gives off carbonic oxide gas, mixed at first with 4 or 5, and at last with 50 per cent. of its volume of carbonic anhydride (altogether a quantity of gas amounting to 33·1 per cent. of the lactic anhydride), and yields a distillate amounting to 90 per cent. of the anhydride, and consisting of *lactide*, $C^6H^8O^4 = 2C^3H^6O^3 - 2H^2O$ (p. 464), which crystallises out on cooling and likewise sublimes, of *lactone* (p 464), with small quantities of acetone, and an odoriferous oil insoluble in water, whilst a quantity of difficultly combustible charcoal remains, amounting to 6·9 per cent. of the anhydride (Pelouze). The anhydride, which remains undecomposed after heating to 240°, gives off, when kept for some time between 250° and 260°, carbonic oxide mixed with 3 or 4 per cent. of its bulk of carbonic anhydride (without any carburetted hydrogen); yields a yellowish distillate, which deposits crystals of lactide, and contains, in addition to the lactide (amounting to 14·9 per cent. of the anhydride), nothing but ordinary lactic acid, citraconic acid, aldehyde (amounting to 12·2 per cent. of the anhydride), but neither acetone nor lactone; and leaves 1 or 2 per cent. of shining, easily combustible charcoal. The aldehyde and the citraconic acid [?] are perhaps merely products of decomposition of the lactide, $C^6H^8O^4 = 2C^2H^4O + 2CO$. The ordinary lactic acid is formed from a portion of the anhydride by addition of the water set free by the conversion of the remainder into lactide. If the anhydride be distilled at 300° instead of 260°, less lactic acid and lactide are obtained, and more aldehyde (Engelhardt). Lactic acid, when heated, gives off pungent vapours which excite coughing, and yields a brown empyreumatic oil, together with an acid liquid, the acid of which is neither lactic nor acetic acid, but forms a viscid uncrystallisable salt with oxide of zinc (Braconnot, Ann. Ch. Phys. l. 375). It yields a watery distillate continually becoming more acid, the first portion of which, however, assumes a syrupy consistence when evaporated *in vacuo*, and if then gently heated in contact with the air, deposits crystals of lactide; it afterwards yields an oil and then a buttery mass, which solidifies in the neck of the retort, and when exhausted with cold ether, leaves scales and ultimately rhombic laminæ. Lastly, there remains a shining, tumefied charcoal. The acid which remains after partial distillation likewise contains a certain quantity of lactide; and on boiling this acid with ether and cooling the liquid, the lactide crystallises out (Corriol). By continued heating to between 180° and 200°, the acid is much more quickly converted into the anhydride, and yields a much more copious distillate of the unaltered acid, than between 130° and 140°;

and if a platinum wire be immersed in the liquid, the lactic acid may be distilled over quite unaltered, and with regular ebullition (Engelhardt). If the lactic acid contains a small quantity of sulphuric acid, it yields only carbonic oxide gas, no carbonic anhydride (Pelouze). If it contains the smallest quantity of impurity, albumen for example, it does not yield any sublimate of lactide (Gay-Lussac and Pelouze). Lactic acid, heated slowly in contact with the air, boils gently, emitting a suffocating odour, swells up, blackens, and leaves a spongy charcoal. (Berzelius.)

2. Lactic acid (or ferrous lactate), mixed with a sixfold quantity of *oil of vitriol*, and gently heated, froths up briskly, acquires a dark-brown colour; gives off about ⅓ of its weight of pure carbonic oxide gas; and at a higher temperature, yields about ⅓ of its weight of a humus-like substance. (Pelouze.)

3. Boiling *nitric acid* converts lactic into oxalic acid. (Jules Gay-Lussac and Pelouze.)

4. Lactic acid and its salts, distilled with small quantities of *common salt*, *peroxide of manganese*, *sulphuric acid*, and water, yield chiefly aldehyde; with larger quantities, principally chloral. (Städeler, Ann. Ch. Pharm. lxix. 332.)

5. With aqueous *alkaline hypochlorites*, or *chlorous acid*, lactic acid is converted, first into oxalic acid, then, with effervescence, into carbonic anhydride. (Cap and Henry.)

6. When treated with *peroxide of barium* or of *lead*, it is converted chiefly into oxalic acid. (Cap and Henry.)

7. Distilled with *dilute sulphuric acid* and *peroxide of manganese* or *peroxide of lead*, it yields a large quantity of aldehyde, together with carbonic anhydride. (Liebig.)

8. Lactate of calcium distilled with *pentachloride of phosphorus*, yields chloride of lactyl $(C^3H^4O)''.Cl^2$:

$$\left.\begin{matrix}C^3H^4O\\H^2\end{matrix}\right\}O^2 + PCl^5 = C^3H^4OCl^2 + PCl^3O + H^2O.$$

9. *Hydriodic acid*, or a mixture of di-iodide of phosphorus with a small quantity of water, reduces lactic acid to propionic acid:

$$\underset{\text{Lactic acid.}}{C^3H^6O^3} + 2H^2 = \underset{\text{Propionic acid.}}{C^3H^6O^2} + H^2O.$$

(Lautemann, Ann. Ch. Pharm. cxiii. 217.)

10. The action of *fuming sulphuric acid* upon lactic acid or lactate of calcium produces di-sulphometholic acid. (Strecker, Ann. Ch. Pharm. cxviii. 291.)

Sarcolactic or **Paralactic Acid.** In 1806, Berzelius discovered an acid in muscular flesh which he believed to be identical with the lactic acid prepared from milk. In 1847, Liebig (Ann. Ch. Pharm. lxii. 278 and 326) showed that this acid, though similar to the acid of sour milk in composition and in many other respects, nevertheless exhibited distinct differences from it in some of its salts. He therefore distinguished it by the name Sarcolactic acid (*Fleischmilchsäure*), in place of which Paralactic acid was proposed by Heintz (Pogg. Ann. lxxv. 391). In 1858, it was found by Strecker (Ann. Ch. Pharm. cv. 313) that, by heating paralactic acid for a long time to 130° or 140° and dissolving the resulting lactic anhydride in water, this acid may be transformed into ordinary lactic acid.

Preparation.—Chopped flesh is exhausted with cold water or dilute alcohol; the infusion is mixed with baryta-water; the albumin is coagulated by boiling, and removed by filtration; and the clear liquid is concentrated by evaporation. Sulphuric acid is added to the syrupy residue, and it is shaken with ether, which then leaves paralactic acid when evaporated.

The difference between sarcolactic and ordinary lactic acids is most distinctly marked in their calcium- and zinc-salts (see below, Lactate of calcium and Lactate of zinc): the acids themselves are hardly to be distinguished.

Thebolactic acid. This is another modification of lactic acid found, by T. and H. Smith, of Edinburgh, in the mother-liquors of the preparation of morphine. Some of its salts are said to differ in certain respects from ordinary lactic acid (see THEBOLACTIC ACID).

Lactates. The best known salts of lactic acid are of the form $C^3H^5MO^3$: there are also acid salts containing $C^3H^5MO^3.C^3H^6O^3$, and double salts, $C^3H^5MO^3.C^3H^5M'O^3$. The existence of these acid and double salts led Gerhardt and other chemists to double the formula of lactic acid, making it $C^6H^{12}O^6$, and regarding the neutral salts as $C^6H^{10}M^2O^6$, and the acid salts as $C^6H^{11}MO^3$. But the relations between lactic and propionic acids have induced chemists in general to return to the lower formula of lactic acid, and to regard the acid lactates as constituted like the acid acetate of potassium (i. 17). Moreover, Wurtz's discovery of the diethylic lactate would render it necessary to regard the acid with the higher formula as tetrabasic, for which there is no warrant.

The crystalline lactates do not effloresce on exposure to the air, but give off water *in vacuo*, and the whole of it at 100°, excepting the acid nickel-salt which retains it till heated to 130°. They sustain a heat of 150° to 170° without decomposition; the zinc-salt may be heated even to 200°. They are for the most part sparingly soluble in cold water, and effloresce rapidly from their solutions: they are all insoluble in ether.

LACTATE OF AMMONIUM.—Obtained by neutralising the acid with ammonia. Forms prismatic crystals which deliquesce and give off ammonia when exposed to the air.

LACTATE OF ANTIMONY.—Oxide of antimony dissolves in lactic acid or in acid lactate of potassium, but does not form a crystalline salt.

LACTATE OF BARIUM.—The *neutral* salt is uncrystallisable and very soluble in water. The *acid salt*, $C^3H^5BaO^3.C^3H^6O^3$, is obtained by adding to a solution of the neutral salt a quantity of lactic acid equal to that which it already contains. It is then deposited in crystals which may be purified by washing with alcohol. It is not altered by exposure to the air or *in vacuo*. It dissolves easily in water. Gives off an aromatic odour at 100°.

LACTATE OF BISMUTH.—Only two basic salts are known: *α*. $2C^3H^5biO^3.bi^2O[bi = \frac{1}{3}Bi]$. This salt is obtained in needles by treating hydrate or carbonate of bismuth with lactic acid, and evaporating. A better mode of preparing it is to mix the concentrated solutions of nitrate of bismuth and lactate of sodium—the latter in slight excess, whereby a crystalline pulp is precipitated consisting of lactate of bismuth mixed with nitre. On redissolving this in a small quantity of water, and leaving the solution at rest, the lactate of bismuth is deposited in crystalline crusts.

β. $C^3H^5biO^3.2bi^2O$.—By proceeding in the manner just described, but with boiling solutions, or by adding nitrate of bismuth drop by drop to a solution of lactate of sodium, the salt *β* is precipitated as a powder unalterable in boiling water. It appears also to be produced by the solution of *α*.

LACTATE OF CADMIUM, $C^3H^5CdO^3$.—Obtained in small needles by dissolving carbonate of cadmium in the acid. When deposited from a boiling solution, it is anhydrous. Insoluble in alcohol.

LACTATES OF CALCIUM.—The *neutral acetate*, $C^3H^5CaO^3.2H^2O$ and $C^3H^5CaO^3.\frac{5}{2}H^2O$, is obtained by saturating a boiling solution of lactic acid with carbonate of calcium, and evaporating the filtered liquid. It is also produced abundantly when a solution of sugar mixed with cheese and carbonate of calcium is left to itself for some weeks at a temperature of 20° to 30° C. According to Corriol, the same salt is deposited from an infusion of *nux vomica* which has fermented for a few days. It is deposited from an aqueous or alcoholic solution in small, very white, mammellated crystals. It dissolves in all proportions in water and in alcohol at the boiling heat, but cold water dissolves only traces of it.

The characters of this salt differ somewhat according as it has been prepared with lactic acid *α* extracted from muscular flesh (sarcolactic acid), or from lactic acid *β*, produced by the fermentation of sugar.

The salt of the acid *α*, deposited from an aqueous solution, contains 2 at. water; that of the acid *β* crystallised in the same way contains 2½ at. ($2C^3H^5CaO^3.5H^2O$). The lactate *α* retains its water of crystallisation at 100° longer than the salt *β* Lastly, the salt *α* requires 12·4 pts. of water to dissolve it; whereas the *β* dissolves in 9·5 pts. Pure lactate of calcium, dried at 100°, and containing $C^3H^5CaO^3$, loses water at 280°, and is converted into dicalcic dilactate, $C^6H^8Ca^2O^6$ (DILACTIC ACID, p. 461). (Wurtz and Friedel.)

Acid lactate of calcium, $C^3H^5CaO^3.C^3H^6O^3.\frac{3}{2}H^2O$, obtained by mixing a solution of the neutral lactate with as much lactic acid as it already contains, forms crystalline masses resembling wavellite. It dissolves in absolute alcohol, gives off its water of crystallisation at 80°, and rapidly turns brown at a higher temperature.

Lactate of calcium and potassium.—Obtained by incompletely precipitating a solution of lactate of calcium with carbonate of potassium. It forms hard crystals soluble in water.

Lactate with chloride of calcium, $C^3H^5CaO^3.CaCl.3H^2O$.—Obtained in prisms by mixing the solutions of the two salts, and concentrating the liquid considerably.

LACTATE OF CHROMIUM is an uncrystallisable salt.

LACTATE OF COBALT, $C^3H^5CoO^3.3H^2O$.—Peach-blossom-coloured needles, nearly insoluble in cold water, moderately soluble in boiling water, insoluble in alcohol. Its solution has a slight acid reaction.

LACTATE OF COPPER, $C^3H^5CuO^3.\frac{3}{2}H^2O$ and H^2O, is obtained by precipitating sulphate of copper with lactate of barium, or by boiling carbonate of copper with lactic acid. By the latter method a basic salt is also produced, from which the product must be purified by recrystallisation or by addition of lactic acid.

Lactate of copper *α* (sarcolactate) crystallises in sky-blue nodules containing 1½ at. water, which it does not give up at 100° till after a considerable time; whereas *β* forms larger crystals, of a green or very dark blue colour, and containing 1 at. water, which they give off by simple desiccation over sulphuric acid. The salt *α* exposed to a gradually increasing heat does not exhibit any change below 210°; but at that temperature it takes fire and burns, leaving a residue of metallic copper. *β* heated in like manner decomposes at 140°, leaving a residue of cuprous oxide. Lastly, *α* dissolves in 1·95 pt. cold water, in 1·24 pt. boiling water, and in a small proportion of alcohol; whereas *β* requires for solution 6 pts. of cold water, 22 pts. boiling water, 115 pts. cold alcohol, and 26 pts. boiling alcohol.

Lactates of Iron.—*Ferrous lactate*, $2C^3H^5FeO^3.3H^2O$, may be prepared by decomposing the calcium-salt with ferrous sulphate, or by mixing lactate of ammonium with ferrous chloride in presence of alcohol; also by boiling dilute lactic acid with iron-filings. It forms small crystals having a slight greenish tint; their solution oxidises but slowly on exposure to the air. This salt is sometimes used medicinally in the treatment of chlorosis.

Ferric lactate is a brown amorphous mass, deliquescent, and very soluble in water.

Lactate of Lead.—By treating carbonate of lead with boiling lactic acid, a neutral liquid is obtained, which when evaporated deposits a mass of small pellicles, and acquires an acid reaction.

Lactate of Magnesium, $C^3H^5MgO^3.2H^2O$ and $\frac{3}{2}$ H^2O.—Obtained by dissolving magnesia in lactic acid. Crystallises in prisms permanent in the air, soluble in water, insoluble in alcohol. The salt *α* (sarcolactate) contains 2 at. water; the salt *β* contains $\frac{3}{2}$ at. The salt *α* is also much more soluble in water and alcohol than *β*.

Lactate of Manganese, $2C^3H^5MnO^3.3H^2O$.—Large, brilliant, amethyst-coloured crystals, moderately soluble in cold water, very soluble in hot water; soluble also in alcohol.

Lactates of Mercury.—*Mercurous lactate*, $C^3H^5HhgO^3.H^2O$. Rose-coloured or crimson crystals, obtained by mixing the boiling solutions of lactate of sodium and mercurous nitrate.

Mercuric lactate.—The neutral salt is not known. A basic salt, $2C^3H^5HgO^3.Hg^2O$, or $C^6H^{10}HhgO^6.HhgO$, is obtained by boiling mercuric oxide with dilute lactic acid till the liquid is saturated. The solution yields by evaporation a yellow salt, insoluble in water, and a colourless salt which is very soluble. The latter, which has the composition above given, crystallises in shining prisms which afforesce rapidly in the air, and are very sparingly soluble in alcohol.

Lactate of Nickel, $2C^3H^5NiO^3.3H^2O$.—Apple-green needles, very soluble in cold water, more soluble in hot water, insoluble in alcohol. The solution has a slight acid reaction. According to Engelhardt, the salt *α* gives off the whole of its water at 100°, but *β* does not part with the third atom before 130°.

Lactate of Potassium.—Very soluble, and crystallises with difficulty.

Lactate of Silver.—$C^3H^5AgO^3.H^2O$. Obtained by boiling carbonate of silver with lactic acid. It forms silky needles grouped in nodules, neutral to test-paper, blackening quickly by exposure to light, very soluble in warm alcohol, nearly insoluble in cold alcohol. The aqueous solution, when boiled for some time, acquires a fine blue colour, and deposits brown flakes. It may be heated to 80° without decomposing, but blackens and gives off gas at 100°. The air-dried salt contains 2 at. water, which it gives off *in vacuo*.

Lactates of Sodium.—*Monosodic lactate*, $C^3H^5NaO^3$. An amorphous, deliquescent mass, very soluble in water and absolute alcohol; ether precipitates it from its alcoholic solution. Dried at 140°, it possesses the above composition. (Wislicenus.)

Disodic lactate.—Monosodic lactate heated to 130° is acted on by sodium, hydrogen being liberated and a sodium-salt formed, which, together with unaltered monosodic lactate, contains disodic lactate. The product thus obtained is a bright yellow, very hard and brittle mass. It deliquesces quickly in the air. When covered with water, it is decomposed, with very perceptible development of heat, into monosodic lactate and hydrate of sodium. The deliquesced salt absorbs carbonic anhydride from the air; so that when it has been long exposed, absolute alcohol dissolves out monosodic lactate, leaving a residue of carbonate of sodium. Disodic lactate appears to dissolve without alteration in perfectly anhydrous alcohol. With iodide of methyl, it yields iodide of sodium and methyl-lactate of sodium. (Wislicenus, Ann. Ch. Pharm. cxxv. 49.)

Lactate of Strontium, $2C^3H^5SrO^3.3H^2O$.—Neutral and very soluble.

Lactate of Tin. *Stannous lactate.* $C^6H^{10}SnO^6.SnO$.—This basic salt is obtained by mixing an acid solution of stannous choride with lactate of sodium. It is a white crystalline powder, insoluble in cold water, very soluble in hydrochloric acid; soluble also in acetic acid after prolonged ebullition.

Stannic chloride mixed with lactate of sodium does not yield crystals, or a precipitate even after concentration to a syrup.

Lactate of Uranium.—Uranic lactate, $C^3H^5(U^2O)O^3$, is obtained in yellow crystalline crusts by evaporating a solution of uranic oxide in lactic acid.

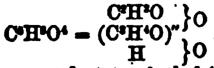
Lactate of Zinc, $C^3H^5ZnO^3.\frac{3}{2}H^2O$ and H^2O.—Prepared by boiling carbonate of zinc with lactic acid. The salt *α* (sarcolactate) is deposited, as the solution cools, in very dilute needles, irregularly grouped; on touching the vessel, these groups separate, and the whole of the liquid solidifies to a pulp. The salt β forms sometimes shining crusts, sometimes large needles irregularly grouped.

The salt α contains 1 at., the salt β $\frac{2}{3}$ at. water, which it gives off quickly at 100°; whereas α requires heating for several hours to dehydrate it completely. β may be heated without alteration to 210°, whereas α begins to give off empyreumatic vapours between 100° and 150°.

The two salts also differ greatly in solubility. α dissolves in 2·88 pts. of boiling and 5·7 pts. of cold water; in 2·23 pts. of cold alcohol, and in about the same quantity with boiling heat. The salt β requires for solution 6 pts. of boiling water, 5·8 pts. of cold water, and is nearly insoluble in alcohol.

According to Liebig, the neutral salt prepared with lactic acid from sourcrout splits up, when its solution is mixed with alcohol, into a basic and an acid salt. Engelhardt did not observe this decomposition of the zinc-salt prepared with lactic acid obtained by the fermentation of sugar.

Derivatives of Lactic acid.

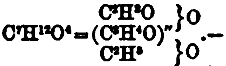


Acetolactic acid. $C^5H^8O^4 = \left.\begin{matrix} C^2H^3O \\ (C^3H^4O)'' \\ H \end{matrix}\right\} O^2$. (Wislicenus, Ann. Ch. Pharm. cxxv. 60.)—Obtained from acetolactate of ethyl (*vid. inf.*) by heating it with water to 150° for two or three hours. It is a thick, syrupy liquid; very easily soluble in water; and has an agreeable, purely acid taste, without any irritating after-taste. It is not volatile without decomposition, but is carried over to a considerable extent by water-vapour; even then, however, it is partially decomposed into acetic and lactic acids. Under all circumstances, indeed, both the acid and its salts readily undergo decomposition into these two acids.

Acetolactate of barium, $C^5H^7BaO^4.2H^2O$.—Acetolactic acid dissolves carbonate of barium, with evolution of carbonic anhydride. The solution is warmed for a very short time with excess of the carbonate, in order to complete the neutralisation (longer heating would cause decomposition into lactate and carbonate); then filtered, and evaporated to a syrup on the water-bath. This syrup becomes a tough mass on cooling, and dries up over sulphuric acid *in vacuo* to a brittle and pulverisable substance resembling gum. It then still retains 2 molecules of water, one of which is given off at 100°, the second only at 140°. Acetolactate of barium is very soluble in water, and dissolves also in absolute alcohol. Ether produces in the alcoholic solution a flocculent precipitate, which soon unites into a tough, sticky mass.

Acetolactate of copper.—Obtained as a blue-green, amorphous, gummy mass, by decomposing the barium-salt with sulphate of copper, and evaporating. It dissolves easily in water and alcohol, and becomes moist when exposed to the air.

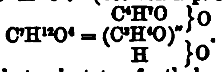
Acetolactate of zinc, $C^5H^7ZnO^4$.—A cold solution of acetolactate of barium is decomposed with an exactly equivalent quantity of sulphate of zinc, and the liquid is evaporated over sulphuric acid without the aid of heat. The gummy mass thus obtained contains imbedded crystals of lactate and acetate of zinc. To separate these, the acetolactate of zinc is dissolved out by a small quantity of absolute alcohol. By evaporating the solution *in vacuo*, the salt is left as a gummy mass, which, when thoroughly dried over sulphuric acid, is not decomposed at 110°. Its solutions, both aqueous and alcoholic, become quickly acid, owing to the extraordinary ease with which the salt decomposes into acetate and lactate of zinc, and acetic and lactic acids.



Acetolactate of ethyl, $C^7H^{12}O^4 = \left.\begin{matrix} C^2H^3O \\ (C^3H^4O)'' \\ C^2H^5 \end{matrix}\right\} O^2$.—Formed by the action of chloride of acetyl on monethylic lactate (p. 463). This reaction, which was first mentioned by Perkin (Zeitschr. Chem. Pharm. 1861, p. 166), has been further investigated by Wislicenus (*loc. cit.* p. 58).

Acetolactate of ethyl is a colourless, mobile liquid, of an agreeable, aromatic smell, recalling that of Calville-apples. It is neutral, and insoluble in water, but is gradually decomposed by it into alcohol and acetolactic acid (see above). It dissolves in alcohol and ether in all proportions, and is precipitated by water from its alcoholic solutions. Boiling point 177°, under 733 mm. pressure. Specific gravity, 1·0458 at 17°, water at the same temperature being taken as unity; vapour-density, found 5·70, calculated 5·54.

Benzolactic acid. $C^{10}H^{10}O^4$. (See vol. i. p. 561.)



Butyrolactic acid. $C^7H^{12}O^4 = \left.\begin{matrix} C^4H^7O \\ (C^3H^4O)'' \\ H \end{matrix}\right\} O^2$. (See vol. i. p. 697.—To the description there given of butyrolactate of ethyl, we add the following particulars.)

Boiling point, 208°. Vapour-density, found 6·73, calculated 6·51. Heated with caustic potash in a sealed tube, it is decomposed into alcohol, and lactate and butyrate of potassium. (Wurtz, Ann. Ch. Phys. [3] lix. 177.—This mode of decomposition is important, since, were Kolbe's view of the constitution of butyrolactic acid correct, it ought to yield propionate and butylactate (oxybutyrate) of potassium when decomposed by potash. (Compare Ann. Ch. Pharm. cxiii. 234, 235, also vol. ii. p. 701 of this work.)

Dilactic acid. *Anhydrous lactic acid* (Pelouze), *Acide lactidique* (Laurent).
$C^6H^{10}O^5 = \left.\begin{matrix}(C^3H^4O)'' \\ (C^3H^4O)'' \\ H^2\end{matrix}\right\}O^3$. This substance remains as a pale-yellow, amorphous, easily fusible mass, when lactic acid is exposed for some time to a temperature between 130° and 200°. It is converted into lactic acid, slowly by ebullition with water, quickly by the action of aqueous alkalis. By dry distillation, it is converted into lactide (p. 464). With gaseous ammonia it yields the compound $C^6H^{14}N^2O^4$, commonly called lactamate of ammonium, but more correctly dilactylamate of ammonium (p. 453).

Dilactate of calcium, $C^6H^8Ca^2O^5$.—Obtained by heating lactate of calcium, previously dried at 100°, to 280°. It is much less soluble in absolute alcohol than lactate of calcium. (Wurtz and Friedel.)

Dilactate of ethyl. Monethylic dilactate, $C^8H^{14}O^5 = \left.\begin{matrix}(C^3H^4O)^2 \\ C^2H^5.H\end{matrix}\right\}O^3$, is formed by the action of chloropropionate of ethyl on lactate of potassium:

$$\underset{\text{Chloropropionate of ethyl.}}{\left.\begin{matrix}(C^3H^4O)'' \\ C^2H^5\end{matrix}\right\}\begin{matrix}Cl \\ O\end{matrix}} + \underset{\text{Lactate of potassium.}}{\left.\begin{matrix}(C^3H^4O)'' \\ HK\end{matrix}\right\}O^2} = \underset{\text{Monethylic dilactate.}}{\left.\begin{matrix}(C^3H^4O)^2 \\ C^2H^5.H\end{matrix}\right\}O^3} + KCl$$

It is a colourless, oily liquid, of specific gravity 1·134 at 0°; boiling point about 235°. It is decomposed, when heated with water in sealed tubes, into alcohol and lactic acid. (Wurtz and Friedel, Ann. Ch. Phys. [3] lxiii. 112.)

MONOSULPHODILACTIC ACID, $C^6H^{10}O^4S$. (Schacht, Ann. Ch. Pharm. cxxix. 4.)—This acid was obtained as the product of an operation conducted with a view to the preparation of sulpholactic acid (p. 462). Instead of neutralising the aqueous solution of the crude product containing sulpholactate of potassium (see p. 462) with hydrochloric acid, it was neutralised with dilute sulphuric acid, and a further quantity of sulphuric acid was then added, sufficient to decompose the sulpholactate only. Monosulphodilactic acid then separated at the surface of the concentrated saline solution, and was obtained pure by solution in ether and evaporation under the air-pump.

Monosulphodilactic acid is soluble in water, alcohol, and ether, but does not crystallise. It contains the elements of two molecules of sulpholactic acid *minus* one molecule of sulphydric acid:

$$2C^3H^6O^2S - H^2S = C^6H^{10}O^4S.$$

By oxidation with dilute nitric acid, it yields dilactylsulphurous acid, $C^6H^{10}SO^7$ (*Dipropionschwefelsäure*, Schacht), the barium-salt of which is a white amorphous powder containing $C^6H^8Ba^2SO^7$.

Ethyl-lactic acid. See LACTIC ETHERS (p. 463).

Lactylsulphurous acid. *Sulphopropionic acid*, $C^3H^6SO^5$.—This acid is formed by the action of fuming sulphuric acid on cyanide of ethyl, or on propionamide, in the process for preparing disulphetholic acid (Buckton and Hofmann, Chem. Soc. Qu. J. ix. 251); also when sulpholactic acid is oxidised with dilute nitric acid. (Schacht.)

Lactylsulphite of Ammonium is exceedingly soluble in water, and uncrystallisable. Absolute alcohol throws it down as a thick treacly mass.

Lactylsulphite of Barium, $C^3H^4Ba^2SO^5$, crystallises from a saturated boiling solution in fine silky crystals, arranged in spherical groups. It may be dried at 170° without decomposition.

DILACTYLSULPHUROUS ACID. See above.

Lactyl- and dilactylsulphurous acids may be regarded as containing the radicles of lactic and sulphurous acids, and may be represented by the following rational formulæ:

$$\underset{\text{Lactylsulphurous acid.}}{\left.\begin{matrix}(C^3H^4O)'' \\ (SO)'' \\ H^2\end{matrix}\right\}O^3} \qquad \underset{\text{Dilactylsulphurous acid.}}{\left.\begin{matrix}(C^3H^4O)'' \\ (C^3H^4O)'' \\ (SO)'' \\ H^2\end{matrix}\right\}O^4}$$

Methyl-lactic acid. See LACTIC ETHERS (p. 464).

Succino-lactic acids. The only known representatives of these substances are diethylic succinolactate, $C^{11}H^{18}O^6$, and diethylic succinodilactate, $C^{14}H^{22}O^8$. *Diethylic succino lactate*, $\left.\begin{matrix}(C^4H^4O^2)'' \\ (C^3H^4O)'' \\ (C^2H^5)^2\end{matrix}\right\}O^3$, is an oily liquid, insoluble in water, boiling at 280°, and of specific gravity 1·119 at 0°, formed by the action of chloropropionic ether on succinate of ethyl and potassium in presence of alcohol. It is decomposed, when heated with baryta-water, into alcohol and succinate and lactate of barium.

Diethylic succinodilactate, $\left.\begin{matrix}C^4H^4O^2 \\ (C^3H^4O)^2 \\ (C^2H^5)^2\end{matrix}\right\}O^4$, is a liquid boiling between 250° and 270°, produced by the action of chloropropionate of ethyl upon succinate of potassium. (Wurtz and Friedel.)

Sulpholactic acid, $C^3H^6O^2S = \left.\begin{matrix}(C^3H^4O)'' \\ H^2\end{matrix}\right\}\begin{matrix}S \\ O\end{matrix}$. (Schacht, Ann. Ch. Pharm. cxxix. 1.)—The potassium-salt of this acid is formed when an intimate mixture of chloropropionate of potassium and sulphydrate of potassium is heated for four or five hours to a little above 100°:

$$\underset{\text{Chloropropionate of potassium.}}{C^3H^4KClO^2} + HKS = \underset{\text{Sulpholactate of potassium.}}{C^3H^5KO^2S} + KCl$$

To prepare the acid, the mixture of chloride, phosphate, and chloropropionate, obtained by neutralising with carbonate of sodium the crude product of the distillation of lactate of calcium with pentachloride of phosphorus, is mixed with sulphydrate of potassium (1 molecule of the latter for each molecule of lactate used), and the solution is evaporated and the residue heated as above. The product of this operation is dissolved in water, saturated with hydrochloric acid, warmed to expel sulphydric acid, largely diluted, made slightly alkaline with ammonia, and precipitated with acetate of lead. The lead-precipitate is thoroughly washed with *cold* water, then decomposed with sulphydric acid, and the filtered liquid repeatedly evaporated to a syrup to remove the hydrochloric acid. The residue is dissolved in water and neutralised at the boiling heat with carbonate of barium, which causes a precipitate of phosphate of barium, while sulpholactate of barium remains in the solution. From this solution the acid is again thrown down as lead-salt; the precipitate is decomposed by sulphydric acid; and the resulting solution of the free acid is concentrated by evaporation on the water-bath.

Sulpholactic acid crystallises in broad needles, grouped together in bundles or brushes; it melts without decomposition below 100°, and solidifies in the crystalline form. It dissolves in water, alcohol, and ether, and may be boiled in dilute solution without decomposing. Nitric acid, not in excess, oxidises it to lactylsulphurous acid, $C^3H^6SO^5$ (*sulphopropionic acid*, Buckton and Hofmann). (*vid. sup.*)

Sulpholactate of barium, $C^3H^5BaO^2S$.—Crystallises in cauliflower-shaped masses; dissolves easily in water, insoluble in alcohol; it is not altered when dried at 100°.

Sulpholactate of lead.—Amorphous, and becomes brown on keeping.

Sulpholactate of potassium is obtained by double decomposition from sulpholactate of barium and sulphate of potassium. The solution evaporated *in vacuo* to a syrup deposits broad plates which are very deliquescent.

Sulpholactate of silver, $C^3H^5AgO^2S$.—A white, amorphous precipitate obtained by adding nitrate of silver to a solution of sulpholactate of barium. It is soluble in nitric acid, and decomposes below 100°.

Trilactic acid. The diethylic ether corresponding to this acid is known. (See LACTIC ETHERS.)

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LACTIC ANHYDRIDE. Dilactic acid (p. 461) was formerly called anhydrous lactic acid, or lactic anhydride. The true lactic anhydride is LACTIDE (p. 464).

LACTIC ETHERS. Owing to its peculiar constitution as a mono-basic diatomic acid, lactic acid is capable of forming three different ethers containing the same monatomic alcohol-radicle. Thus there are three lactates of ethyl, which may be represented by the following formulæ:

$$\begin{matrix}H \\ (C^3H^4O)'' \\ H\end{matrix}\begin{matrix}\}O \\ \}O\end{matrix}$$

Lactic acid.

$$\begin{matrix}C^2H^5 \\ (C^3H^4O)'' \\ H\end{matrix}\begin{matrix}\}O \\ \}O\end{matrix}$$

Ethyl-lactic acid,

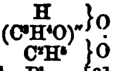
$$\begin{matrix}H \\ (C^3H^4O'' \\ C^2H^5\end{matrix}\begin{matrix}\}O \\ \}O\end{matrix}$$

Monethylic lactate.

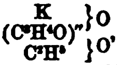
$$\left.\begin{matrix}C^2H^5 \\ (C^3H^4O)'' \\ C^2H^5\end{matrix}\right\}\begin{matrix}O \\ O\end{matrix}$$

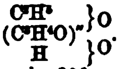
Diethylic lactate.

Of these compounds it will be seen that two—namely, ethyl-lactic acid and monethylic lactate—are isomeric, each being represented by the empirical formula $C^5H^{10}O^3$. The nature of the difference between these bodies will become apparent from the following considerations:—Lactic acid contains one atom of hydrogen, which is readily replaceable by its equivalent of an electro-positive metal by the ordinary processes of saline double decomposition, the result of this replacement being an ordinary metallic lactate: similarly, this atom of hydrogen can be replaced by its equivalent of an alcohol radicle by the ordinary processes of etherification, the result being a neutral ether, which, like compound ethers in general, can be decomposed into alcohol and alkaline lactate by the action of alkalis. But lactic acid contains also another atom of hydrogen, which, by various processes, can be removed, together with an atom of oxygen, the two being replaced by Cl, H^2N, or other similar residues, and is therefore spoken of in the language of the theory of types as existing outside the radicle of the acid, although it cannot be replaced by metals or alcohol radicles in the same manner as the saline hydrogen-atom just referred to. The replacement of this second atom of hydrogen can, however, be effected by other means than those usually employed for the production of normal salts or ethers; and when this is done, the resulting products differ essentially from those obtained by effecting a similar substitution in the case of the saline atom of hydrogen. Thus, monethylic lactate results from the substitution of the radicle C^2H^5 for the saline hydrogen-atom of lactic acid, and ethyl-lactic acid from the substitution of the same radicle for the second of the two hydrogen-atoms existing outside the radicle of the acid. The degree of difference in the properties of these two compounds, resulting from the mode of combination of the alcohol- and acid-residues in each, will be seen by the special description of them which follows. (See also GLYCOLLIC ETHERS, ii. 914–916.)

Lactates of ethyl. MONETHYLIC LACTATE. *Lactic Ether.* $C^5H^{10}O^3 =$  $\left.\begin{array}{c}H\\(C^3H^4O)''\\C^2H^5\end{array}\right\}\begin{array}{l}O\\ \\O\end{array}$ (Strecker, Ann. Ch. Pharm. xci. 352.—Wurtz and Friedel, Ann. Ch. Phys. [3] lxiii. 102.) *Preparation.*—1. One part of lactate of calcium and potassium (p. 458) is distilled with 1·4 pt. ethyl-sulphate of potassium; the thin, faintly-smelling distillate, which passes over between 150° and 180°, is saturated with chloride of calcium, and the syrupy solution is cooled. Crystals are then obtained consisting of $CaCl.2(C^5H^{10}O^3)$; and these by distillation yield tolerably pure lactic ether (Strecker).—2. Syrupy lactic acid, heated to 170° with absolute alcohol, yields monethylic lactate very readily. (Wurtz and Friedel.)

Properties.—A colourless liquid of specific gravity 1·0542 at 0°, and 1·042 at 13°. It has a faint smell, and boils at 156° under a barometric pressure of 753 mm. Vapour-density found, 4·14 (Wurtz and Friedel); calculated, 4·07. Soluble in all proportions in water, alcohol, and ether.

Decompositions.—1. Lactic ether soon becomes acid by contact with *water*, from the formation of alcohol and lactic acids. *Alkalis*, *alkaline earths*, and *oxide of zinc* decompose it in the same manner as water.—2. *Potassium* dissolves in lactic ether with evolution of hydrogen, and forms potassio-lactate of ethyl, $C^5H^9KO^3 =$  $\left.\begin{array}{c}K\\(C^3H^4O)''\\C^2H^5\end{array}\right\}\begin{array}{l}O\\ \\O\end{array}$, isomeric with ethyl-lactate of potassium (*vid. infr.*). This substance forms a viscid mass: treated with iodide of ethyl, it yields iodide of potassium and diethylic lactate (p. 464).—3. Lactic ether, mixed with alcoholic *ammonia*, and evaporated, yields crystals of lactamide (p. 453).

ETHYL-LACTIC ACID. *Valerolactic acid*, $C^5H^{10}O^3 =$  $\left.\begin{array}{c}C^2H^5\\(C^3H^4O)''\\H\end{array}\right\}\begin{array}{l}O\\ \\O\end{array}$. (Wurtz, Ann. Ch. Phys. [3] lix. 171.—Butlerow, Ann. Ch. Pharm. cxiv. 206; cxviii. 325; Bull. Soc. Chim. Paris, 1861, p. 9.) The potassium- and calcium-salts of this acid are obtained as products of the decomposition of diethylic lactate with potash and milk of lime. The acid is also produced (together with iodide of methylene and acrylic acid) by the action of ethylate of sodium on iodoform.

Ethyl-lactic acid is a colourless, somewhat viscid liquid, of a purely sour taste. It boils between 195° and 198°, undergoing partial decomposition at the same time. Water, alcohol, and ether dissolve it in all proportions; but on addition of chloride of calcium or sulphate of sodium to the aqueous solution, it separates as an oil. It becomes more viscid, but does not solidify, in a mixture of salt and snow. Ethyl-lactic acid decomposes the carbonates with effervescence. It cannot be resolved into lactic acid and alcohol by the action of alkalis; but when heated with concentrated hydriodic acid, it yields lactic acid and iodide of ethyl.

The ethyl-lactates are for the most part very soluble, and difficult to obtain in the crystalline form. The *calcium-salt*, $C^5H^9CaO^3$, crystallises by slow evaporation of its aqueous solution in colourless, prismatic crystals, united into stellate groups. Alcohol dissolves it less readily than water, and deposits it in wart-shaped masses. The *silver-salt*, $C^5H^9AgO^3$, crystallises from hot water in bunches of needles of a silky lustre: treated with iodide of ethyl, it yields diethylic lactate. The *zinc-salt* dries up to a gummy mass.

Diethylic Lactate, *Ethyl-lactate of ethyl.*—$C^7H^{14}O^3 = \left.\begin{matrix}C^2H^5\\(C^3H^4O)''\\C^2H^5\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$. (Wurtz, Ann. Ch. Phys. [3] lix. 169.—Wurtz and Friedel, *ibid.* lxiii. 103.—Butlerow, Ann. Ch. Pharm. cxviii. 328). This substance, which may be regarded as the ether of the acid last described, is produced:—1. By the action of ethylate of sodium on chloropropionate of ethyl (*éther chlorolactique*, Wurtz).—2. By the action of iodide of ethyl on ethyl-lactate of silver.—3. By the action of iodide of ethyl on potassio-lactate of ethyl.

Diethylic lactate is a transparent, mobile liquid, of an agreeable ethereal odour. It boils at 156·5° under a pressure of 757 mm. Its specific gravity at 0° is 0·9203; vapour-density, found, 5·052 (calculated, 5·055).

It is insoluble in water, but soluble in alcohol and ether. By ebullition with alkalis, it is transformed into alcohol and an ethyl-lactate (*vid. supr.*); treatment with ammonia converts it into lactamethane (p. 452); it unites directly with lactide, forming diethylic trilactate.

Chlorolactic Ether, *Éther chlorolactique.* Syn. with *Chloropropionate of ethyl* (see Propionic Ethers).

Dilactate of Ethyl. See Dilactic acid (p. 461).

Diethylic Trilactate, $C^{13}H^{22}O^7 = \left.\begin{matrix}(C^3H^4O)^3\\(C^2H^5\ )^2\end{matrix}\right\}O^4$. A thick, colourless liquid, boiling about 270°, formed by heating diethylic lactate to 170° for several days with lactide. Potash decomposes it into alcohol and lactic acid. A substance which appears to be monethylic trilactate, $C^{11}H^{18}O^7 = \left.\begin{matrix}(C^3H^4O)^3\\C^2H^5.H\end{matrix}\right\}O^4$, is obtained as a secondary product in the preparation of diethylic trilactate. (Wurtz and Friedel).

Lactates of Methyl. Methyl-lactic Acid, $C^4H^8O^3 = \begin{matrix}CH^3\\(C^3H^4O)''\\H\end{matrix}\begin{matrix}\}\\ \\ \}O\end{matrix}$, is the only compound belonging to this class that has hitherto been described. It is obtained by heating disodic lactate (p. 459) to 110° or 120° with iodide of methyl. *Methyl-lactate of silver*, $C^4H^7AgO^3$, remains as a brittle, amorphous, gummy mass, when its aqueous solution is evaporated *in vacuo*. *Methyl-lactate of zinc* is very soluble in water, and uncrystallisable; it dissolves also in absolute alcohol. (Wislicenus, Ann. Ch. Pharm. cxxv. 53. G. C. F.

LACTIDE. (True) *Lactic anhydride.* $C^3H^4O^2 = C^3H^4O.O$. (J. Gay-Lussac and Pelouze, Ann. Ch. Pharm. vii. 43; Pelouze, *ibid.* liii. 116; Engelhardt, *ibid.* lxx. 243; Wurtz and Friedel, Ann. Ch. Phys. [3] lxiii. 101.)—Produced by the dry distillation of lactic acid. To prepare it, the product obtained by slowly distilling lactic acid is evaporated at 100°, and the residue washed with cold alcohol, and crystallised from boiling alcohol. Lactide crystallises in rhomboidal plates of dazzling whiteness. It is inodorous; melts at 107°, and begins to boil at 250°, giving off white, irritating vapours, which sublime without alteration, and condense in crystals on cold bodies. It is only slightly soluble in hot water, but is gradually converted into lactic acid by ebullition with water, and quickly by the action of bases.

Ammonia converts it into lactamide (p. 453); ethylamine, into lactethylamide (p. 453). It unites with diethylic lactate, forming diethylic trilactate (*vid. supr.*).

G. C. F.

LACTIDIC ACID. Laurent's name for Dilactic Acid (p. 461).

LACTIN and **LACTOSE.** Syn. with Sugar of Milk.

LACTONE, $C^5H^8O^2$.—A liquid possessing an aromatic smell, and boiling at about 92°, produced, together with lactide, by the dry distillation of lactic acid. (Pelouze, Ann. Ch. Phys. [3] xiii. 262.)

LACTUCA SATIVA. The common lettuce. This plant yields, according to T. Richardson (Jahresber. 1847–48, No. 134, Table to p. 1074), 0·87 per cent. ash, containing:

K^2O	Na^2O	Ca^2O	Mg^2O	SO^3	SiO^2	P^2O^5	Ferric phosphate	NaCl	
46·01	5·29	6·05	2·17	3·89	20·23	8·52	trace	7·82	= 99·98

LACTUCARIUM. A brownish viscid substance obtained by evaporating the juice which exudes, by incision, from the leaves and stems of certain species of *Lactuca*, especially *Lactuca virosa*. It has a peculiar odour resembling that of opium, and acts as a narcotic. German lactucarium contains, according to **Ludwig** (Arch. Pharm. [2], 7, 129; Jahresber. 1847–8, p. 824), from 44·4 to 53·5 per cent. lactucone; a soft resin; about 4 per cent. of an easy fusible waxy body; lactucin, the chief active principle of the substance; lactucic acid; about 1 per cent. of oxalic acid; a non-volatile not bitter acid, which reduces oxide of silver; and a volatile acid smelling like valerianic acid, both in small quantity only; about 7 per cent. of albumin; at least 2 per cent. mannite; a small quantity of a neutral, not bitter, unfermentable substance, crystallising in rhombic pyramids; and from 3 to 6 per cent. ash, containing potash, soda, manganic oxide, ferric oxide, and a small quantity of lime.

LACTUCERIN. A substance, insoluble in water, contained in lactucarium, probably identical with lactucone.

LACTUCIC ACID. This substance is obtained by triturating lactucarium with an equal weight of dilute sulphuric acid, adding 5 pts. of alcohol of 84 per cent., filtering, shaking up the filtrate with slaked lime, decolorising with animal charcoal, evaporating, heating the residue to boiling with a large quantity of water, and evaporating the aqueous solution, after decolorising it with animal charcoal. A mixture of lactucic acid and lactucin then remains, and on dissolving this in boiling water, the lactucin crystallises out on cooling, and the remaining liquid yields, by evaporation, impure lactucic acid.

Lactucic acid thus obtained is a light yellow mass, amorphous at first, but becoming crystalline after a while; its colourless aqueous solution is coloured wine-red by alkalis, and when boiled with cupric sulphate and excess of soda, reduces the cupric to cuprous oxide. (**Ludwig**, Jahresber. 1847–48, p. 824.) According to **Walz** (N. Jahrb. Pharm. xv. 118), it is $C^{40}H^{36}O^{19}$.

LACTUCIN. A substance contained in lactucarium, and supposed to be its active principle. It is obtained by treating the extract with alcohol containing 2 per cent. of strong vinegar, diluting the solution with water, precipitating with basic acetate of lead, removing the excess of lead from the filtrate by sulphydric acid, evaporating at a gentle heat, digesting the residue in ether, and leaving the ethereal solution to evaporate. **Ludwig** and **Kromayer** (Arch. Pharm. [2] cxi. 1) prepare it by macerating lactucarium in 1½ pt. hot water for four days, then pressing the mass, again treating it with a little cold water, boiling it five times with fresh portions of alcohol (which leaves lactucone undissolved), and evaporating the extracts to half the bulk of the material used. The product is then precipitated with basic acetate of lead, and recrystallised from alcohol as above.

Lactucin is yellowish, fusible, bitter, soluble in 80 parts of cold water, moderately soluble in alcohol and in acetic acid, less soluble in ether, which deposits it by evaporation in the crystalline state. According to **Kromayer** (Arch. Pharm. [2] cv. 3), it crystallises in nacreous scales or rhombic tables, probably containing $C^{22}H^{24}O^{7}$ or $C^{22}H^{26}O^{8}$. According to **Walz** (N. Jahrb. Pharm. xv. 118), it is $C^{40}H^{44}O^{18}$. Nitric acid, of specific gravity 1·48, converts it into a resinous body quite devoid of taste. Strong sulphuric acid turns lactucin brown. Lactucin heated with potash gives off ammoniacal products (?). Its solutions are not precipitated by any reagent. (**Buchner**, Rep. Pharm. xliii. 1, Gm. xvi. 276.)

LACTUCONE. $C^{40}H^{64}O^{3}$ (?).—A crystalline substance extracted from lactucarium by boiling alcohol. It forms mammillated crystals, which, after purification by recrystallisation and treatment with animal charcoal, are colourless, insipid, melt between 150° and 160°, are insoluble in water, but dissolve very easily in alcohol, ether, and oils, both fixed and volatile. It yields acetic acid in large quantity by distillation. It may, however, be partly volatilised without decomposition in a stream of carbonic acid gas. It yields by analysis 80·56—81·25 per cent. carbon, and 10·91—11·33 hydrogen, numbers which agree nearly with the formula $C^{40}H^{64}O^{3}$. It is an indifferent substance, and is not affected by potash or by chlorine. Its alcoholic solution does not precipitate metallic salts dissolved in alcohol. (**Lenoir**, Ann. Ch. Pharm. lix. 83.)

LACTUCOPICRIN. An uncrystallisable substance, which remains in the mother-liquors of the preparation of lactucin by **Ludwig** and **Kromayer's** process (*vid. sup.*), after the greater part of that substance has been precipitated by basic acetate of lead. When freed from admixed lactucin and lactucone by ether, it forms a brown, amorphous, very bitter mass, having a faint acid reaction, soluble in water and alcohol. It contains 52·6 per cent. carbon, 6·8 hydrogen, and 36·6 oxygen, agreeing nearly with the formula $C^{22}H^{32}O^{10.5}$, and is therefore produced from lactucin by assumption of water and oxygen. (**Kromayer**, *Die Bitterstoffe*, Erlangen, 1861, p. 79.)

LACTYL, CHLORIDE OF. *Chloride of chloropropionyl.* $C^3H^4OCl^2 = C^3H^4ClO.Cl.$ (Wurtz, Ann. Ch. Phys. [3] lix. 163.—Ulrich, Chem. Soc. Qu. J. xii. 23.)—Obtained, together with oxychloride of phosphorus, by gently heating a mixture of well-dried lactate of calcium with twice its weight of pentachloride of phosphorus. It is difficult to separate the whole of the oxychloride of phosphorus, but the chloride of lactyl may be obtained nearly pure by distilling the liquid, which passes over during the reaction in small quantities at a time, and collecting separately the portion which distils above 140°. Chloride of lactyl is also formed by the direct combination of ethylene and oxychloride of carbon. (Lippmann.)

When freshly prepared, chloride of lactyl is a colourless liquid, but it soon becomes dark coloured, giving off hydrochloric acid. Its boiling point seems to be above 140°, but it is partially decomposed when distilled, the thermometer rising to 180° or 190°.

It sinks to the bottom of *water* and gradually dissolves, forming hydrochloric and chloropropionic acids (PROPIONIC ACID, DERIVATIVES OF) (Ulrich). With absolute *alcohol*, it reacts very energetically, forming hydrochloric acid, chloride of ethyl, and chloropropionate of ethyl. (Wurtz's *éther chlorolactique.*) G. C. F.

LAGONITE. A ferric borate, $Fe^4O^3.B^2O^3.3H^2O$, occurring as an incrustation in the Tuscan lagoons. (Bechi, Sill. Am. J. [2] xvii. 129.)

LAKE. This term is used to denote a species of pigment formed by precipitating colouring matters with some earth or metallic oxide. The principal red lakes are the *Carmine*, *Florence*, and *Madder lakes.*

For the preparation of carmine-lake, four ounces of finely pulverised cochineal are poured into 4 or 6 quarts of rain or distilled water (which has been previously boiled in a pewter kettle), and boiled with it for six minutes longer (it is sometimes recommended to add, during the boiling, two drachms of pulverised cream of tartar). Eight scruples of Roman alum in powder are then added, and the whole is kept upon the fire for one minute longer. As soon as the coarse powder has subsided, and the decoction has become clear, the latter is carefully decanted into large cylindrical vessels, covered over and kept undisturbed, till a fine powder settles to the bottom. From the decanted liquor, which is still much coloured, the rest of the colouring matter may be separated by means of tin-solution: it then yields a carmine-lake but little inferior to the other.

For the preparation of Florentine lake, the sediment of cochineal remaining on the kettle after the preparation just described may be boiled with the requisite quantity of water, the red liquor which remains after the preparation of the carmine likewise mixed with it, and the whole precipitated with the solution of tin. The red precipitate must be frequently washed with water. Exclusively of this, two ounces of fresh cochineal, and one of crystals of tartar, are to be boiled with a sufficient quantity of water, poured off clear, and precipitated with the solution of tin, and the precipitate washed. At the same time, two pounds of alum are also to be dissolved in water, precipitated by caustic potash, and the white earth repeatedly washed with boiling water. Finally, both precipitates are to be mixed together in the liquid state, put upon a filter, and dried. For the preparation of a cheaper sort, one pound of Brazil wood may be employed in the preceding manner, instead of cochineal.

For the following process for making a *lake from madder*, the Society of Arts voted their gold medal to Sir H. C. Englefield. Enclose two ounces troy of the finest Dutch crop madder in a bag of fine and strong calico, large enough to hold three or four times as much. Put it into a large marble or porcelain mortar, and pour on it a pint of clear soft water, cold. Press the bag in every direction, and pound and rub it about with a pestle, as much as can be done without tearing it, and when the water is loaded with colour, pour it off. Repeat this process till the water comes off but slightly tinged, for which about five pints will be sufficient. Heat all the liquor in an earthen or silver vessel, till it is near boiling, and then pour it into a large basin, into which a troy ounce of alum dissolved in a pint of boiling soft water has been previously put. Stir the mixture together, and while stirring, pour in gently about an ounce and half of a saturated solution of carbonate of potassium. Let it stand till cold to settle; pour off the clear yellow liquor; add to the precipitate a quart of boiling soft water, stirring it well; and when cold, separate by filtration the lake, which should weigh half an ounce. If less alum be employed, the colour will be somewhat deeper; with less than three-fourths of an ounce, the whole of the colouring matter will not unite with the alumina. Fresh madder root is equal, if not superior, to the dry.

Almost all vegetable colouring matters may be precipitated into lakes, more or less beautiful, by means of alum or oxide of tin. U.

Yellow lakes are prepared chiefly with decoctions of the berries of various species of *Rhamnus*, also of fustic, weld, quercitron, &c.; the decoctions, mixed with carbonate of potassium in greater or smaller quantity as the colour is to be lighter or darker, being poured into a hot solution of alum quite free from iron. The colour may be heightened by treating the still moist precipitate with tin-solution.—As many of the preceding solutions contain a large quantity of tannin, it is usual, in order to obtain a fine yellow-lake from them, to mix them, in the first instance, with a considerable quantity of sour milk, which precipitates the tannin.

An orange-yellow lake is obtained in like manner by precipitating turmeric or annatto, dissolved in potash with alum. A common kind of yellow-lake is obtained by mixing yellow-lake, prepared as above, with clay, marl, or chalk; better, however, by boiling 5 pts. of crushed yellow berries with 25 to 30 pts. water containing 1 pt. of alum, pouring the clear liquid on 3 or 4 pts. of pounded chalk, and leaving it for several days, stirring frequently, then decanting the liquid, and washing and drying the precipitate. If a greenish tint is desired, a small quantity of burnt or slaked lime may be added.

Blue lakes are but seldom prepared, since Prussian-blue, ultramarine, cobalt-blue, &c., and indigo-carmine answer every purpose for which they could be required. If indigo-carmine be prepared by saturating the solution of sulphindigotic acid with magnesia or its carbonate, instead of potash, it is obtained of a still finer colour. Sometimes a dilute solution of sulphindigotic acid is mixed with alum-solution, and the mixture is precipitated with carbonate of potassium, whereby a peculiar blue lake is obtained. A solution of logwood mixed with alum yields a violet, and, on addition of sulphate of copper, a blue-lake, if the solutions are precipitated in the cold with carbonate of potassium.

Green lakes are usually prepared by mixing blue and yellow lakes. A very good green lake is obtained directly by exhausting 1 lb. of bruised coffee-berries with 10 lbs. of water, and dissolving in the liquid from 2½ to 3 lbs. of sulphate of copper. The clear liquid is precipitated with caustic potash, the coffee-extract being kept in excess to prevent the precipitation of free cupric oxide. The precipitate, which weighs about as much as the coffee-berries used, is moistened with a small quantity of vinegar, and left for some time exposed to the air, whereby its colour is heightened.

LAMINARIA. See SEAWEED.

LAMPADITE. Syn. with WAD.

LAMP-BLACK. Finely-divided carbon, obtained by collecting the smoke of an oil-lamp, or that of burning-pitch or resin. (See CARBON, i. 760.)

LANA PHILOSOPHICA. An old name for the snowy flakes of white oxide which rise and float in the air when zinc is burned.

LANARKITE. A sulphato-carbonate of lead, $Pb^2SO^4.Pb^2CO^3$, or $\left.\begin{matrix}(SO^2)''\\(CO)''\\Pb^4\end{matrix}\right\}O^4$, occurring sometimes in monoclinic crystals, cleavable in two directions, sometimes massive or in flexible laminæ, at Leadhills, Scotland, in Siberia, at Tanné in the Hartz, and at Biberweier, Tyrol. Hardness = 2 to 2·0. Specific gravity = 6·3 to 7. Lustre of cleavage-faces, pearly; of others, adamantine, inclining to resinous. Streak white. Colour, greenish-white, pale-yellow, or grey. Transparent or translucent. Contains, according to Brooke's analysis (Ed. Phil. J. iii. 17), 53·5 per cent. sulphate, and 46·85 carbonate of lead, which is very near the calculated composition. Before the blowpipe it melts to a globule, which becomes white on cooling. Dissolves in nitric acid without perceptible effervescence.

LANCASTERITE. A mineral consisting of a mixture of brucite and hydromagnesite, found near Texas, Lancaster County, Pennsylvania (Dana, ii. 457).

LANTANURIC ACID. (*Lantalic acid*, Laurent.) A product, according to Schlieper (Ann. Ch. Pharm. lvii. 216), of the oxidation of uric acid, by a mixture of ferricyanide of potassium and potash. The result of the process, which is somewhat complicated, is impure lantanurate of potassium, which is dissolved in water, mixed with acetate of lead, and filtered from the precipitated oxalate of lead; the lantanurate of lead then precipitated from the filtrate by ammonia, washed, suspended in water, and decomposed by sulphuretted hydrogen. The filtrate, on evaporation, yields lantanuric acid as a gummy mass, easily soluble in water, insoluble in alcohol: its solution reddens litmus. It appears to be a dibasic acid. It forms a normal- and an acid potassium-salt, the former of which is syrupy, the latter crystallisable. The solution of either of these salts gives, with ammoniacal acetate of lead, a white precipitate, insoluble in cold water and alcohol, soluble in acetic acid or basic acetate of lead.—With ammoniacal nitrate of silver, the acid potassium-salt gives a white precipitate, containing 52·93 per cent. silver.

Schlieper states the formula of the lead-salt to be $C^3H^2Pb^2N^2O^3$, whence that of the acid is $C^3H^4N^2O^3$. Laurent proposes to double the formula. According to Gerhardt (*Traité*, i. 528), lantanuric acid is probably identical with allanturic acid. F. T. C.

LANTHANITE. Native carbonate of lanthanum (and didymium) $(La^2, Di^2)CO^3.3H^2O$, formerly called *carbonate of cerium*. (See CARBONATES, i. 785.)

LANTHANUM. *Atomic weight*, 46·4; *Symbol*, La: or, *Atomic weight*, 92·8; *Symbol*, Lla. This metal appears to be constantly associated with cerium and didymium. Mosander showed in 1839 (Pogg. Ann. xlvi. 648; xlvii. 207) that the red-brown oxide obtained from cerite in the manner described under CERIUM (i. 831), and originally regarded as the oxide of a single metal, contained the oxide of another metal which he called lanthanum (from λανθανειν, because it had previously been concealed in the oxide of cerium); and subsequently, in 1841 (Pogg. Ann. lvi. 504), he discovered that this supposed oxide of a single metal, lanthanum, was really a mixture of the oxides of two distinct metals, for one of which the name lanthanum was retained, while the other was called didymium (διδυμοι, twins).

The separation of lanthanum and didymium from cerium may be effected by either of the methods described under cerium (i. 831, 832). The second and third are easier and more expeditious than the first. If the solution obtained by treating the crude red-brown oxide with dilute nitric acid be evaporated to dryness, and the residue treated with nitric acid diluted with at least 200 pts. of water, a solution will be obtained quite free from cerium (Marignac). Boiling the red-brown oxide with chloride of ammonium also yields a solution of lanthanum and didymium free from cerium. In both cases, however, it is best to test a portion of the solution for cerium by precipitating with excess of caustic potash, and passing chlorine through the solution. The presence of cerium, even in a very small quantity, will be indicated by the formation of a yellow precipitate, after the liquid, supersaturated with chlorine, has been left in a close vessel for several hours.

Holzmann, (J. pr. Chem. lxxv. 321; Rép. Chim. pure, i. 241), prepares pure lanthanum-salts from the liquid which remains after the precipitation of basic ceric sulphate in Bunsen's process for the separation of cerium (i. 832). This liquid, which contains both lanthanum and didymium, is evaporated (during which process a large additional quantity of cerium separates as basic sulphate) and heated till the greater part of the free acid is expelled. The sulphates of lanthanum and didymium, which then separate out, are dissolved in water containing a little nitric acid, and the solution, together with the mother-liquor, is precipitated with oxalic acid; the precipitate, mixed with an equal weight of *magnesia alba*, is heated for some time to low redness; the resulting dark brown oxide is digested with small quantities of dilute nitric acid, which dissolves scarcely anything but the oxides of lanthanum, didymium and magnesium; and the filtrate is boiled for some time with magnesia to separate the last traces of cerium. The liquid is then again precipitated with oxalic acid; the dried and ignited precipitate dissolved in dilute nitric acid; the solution precipitated by sulphate of potassium; the precipitated lanthano- and didymio-potassic sulphates digested with dilute carbonate of sodium, and the resulting carbonates dissolved in dilute sulphuric acid.

A solution free from cerium having been obtained, the separation of the lanthanum and didymium is effected by the different solubilities of their sulphates. To convert them into sulphates, if not already in that form, the solution is treated with excess of a caustic alkali, and the washed precipitate dissolved in dilute sulphuric acid. The mode of proceeding varies according as the lanthanum or the didymium is in excess.

1. When the lanthanum is in excess, in which case the solution has but a faint amethyst tinge, the liquid is evaporated to dryness, and the residue heated in a platinum dish to a temperature just below redness, to drive off the excess of acid, and render the sulphates perfectly anhydrous. The residue is then dissolved in rather less than six times its weight of water, at about 2° or 3° C. (36° F.), the salt being reduced to powder and added in successive small portions, and the vessel containing the liquid being immersed in ice-cold water. Without these precautions, the temperature of the liquid may be raised several degrees, in consequence of the heat evolved by the combination of the anhydrous sulphates with water; and, in that case, crystallisation will commence, and rapidly extend through the whole mass of liquid, as these sulphates are much less soluble in warm than in cold water; but if the liquid be properly cooled, the whole dissolves completely. The solution is next to be heated in the water-bath to about 40° C. (104° F.); the sulphate of lanthanum then crystallises out, accompanied by only a small quantity of sulphate of didymium. To purify it completely, it is again rendered anhydrous, re-dissolved in ice-cold water., &c., and the entire process repeated ten or twelve times. The test of purity is perfect whiteness, the smallest quantity of didymium imparting an amethyst tinge (Mosander). This process succeeds best when a considerable quantity of the mixed sulphates is operated on.

2. When the didymium-salt is in excess, in which case the liquid has a decided rose-colour, separation may be effected by leaving the solution containing excess of acid, in a warm place for a day or two. The sulphate of didymium then separates in large rhombohedral crystals modified with numerous secondary faces; and, at the same time, slender, needle-shaped, violet-coloured crystals are formed, containing the two sulphates mixed. The rhombohedral crystals, which are nearly free from lanthanum, are

removed, and the needles, together with the mother-liquid, treated as in the first method, to obtain sulphate of lanthanum. (Mosander.)

In both cases, the separation may be greatly facilitated by first dissolving the mixed oxides of the two metals in a large excess of nitric acid, and precipitating in successive portions by oxalic acid; the first precipitates thus formed have a much deeper rose-colour, and are much richer in didymium than the latter. The separation thus effected is very imperfect in itself, but it greatly facilitates the subsequent separation of the sulphates, which is much more rapid when one of the sulphates is in great excess with regard to the other. (Marignac.)

Metallic lanthanum is obtained by decomposing the anhydrous chloride with sodium, and dissolving out the chloride of sodium with alcohol of specific gravity 0·833. It is a dark, lead-grey powder, soft to the touch, and adhering when pressed.

Lanthanum appears to form only one series of compounds, in which it is mono- or diatomic, according to the atomic weight adopted, *e.g.* the *chloride* $LaCl$ or $LlaCl^2$; the *protoxide* La^2O or $LlaO$.

LANTHANUM, CHLORIDE OF, $LaCl$, is obtained in the anhydrous state by igniting the oxide in a current of hydrochloric acid gas (Mosander), or by dissolving the oxide in hydrochloric acid, evaporating the solution, mixed with sal-ammoniac, to dryness, and heating the residue till the sal-ammoniac is expelled. It then remains as a radio-crystalline mass, which deliquesces in moist air, and dissolves easily in alcohol. (R. Hermann, J. pr. Chem. lxxxii. 385.)

A *hydrated chloride*, $LaCl.2H^2O$, is obtained as a radio-crystalline mass, by evaporating a solution of the oxide to a syrup, and leaving it over oil of vitriol. When heated in moist air, it gives off water and hydrochloric acid, leaving a mixture of chloride of lanthanum and an oxychloride containing $3La^2O.2LaCl$.

Chloromercurate of Lanthanum, $LaCl.3HgCl.4H^2O$, is obtained by evaporating a solution of the component chlorides, in colourless cubes, easily soluble in water, but not deliquescent. (Marignac, Ann. Min. [5] xv. 272.)

LANTHANUM, DETECTION and ESTIMATION OF. 1. *Reactions.* Pure lanthanum-compounds fused with borax before the blowpipe, form a perfectly colourless bead; the slightest tinge of amethyst is an indication of the presence of didymium.

Lanthanum-salts in solution are colourless, and have an astringent taste. With caustic *potash* or *soda*, they yield a white bulky gelatinous precipitate of the hydrated oxide, which is insoluble in excess of the alkali, but dissolves completely in chlorine-water, without forming any yellow deposit. *Ammonia* throws down a basic salt. *Oxalic acid* or *oxalate of ammonium* forms a white flocculent precipitate, which does not become crystalline. In other respects the solutions resemble those of cerous salts (i. 833), especially in forming with sulphate of potassium a white crystalline precipitate quite insoluble in excess of the reagent.

2. *Estimation and Separation.*—Lanthanum is best precipitated from its solutions by oxalate of ammonium. The precipitated oxalate, ignited in a covered platinum crucible, is converted into the anhydrous oxide, La^2O, containing 85·4 per cent. of the metal.

The methods of separating lanthanum from most other metals are the same as those adopted for cerium and didymium. The separation of lanthanum from cerium itself may be effected by precipitation with an alkaline hypochlorite, or by boiling the mixed oxides in a solution of sal-ammoniac (i. 832). No method of separating lanthanum from didymium, sufficiently exact for quantitative analysis, has yet been discovered.

3. *Atomic Weight of Lanthanum.*—Mosander, by the analysis of sulphate of lanthanum, estimated the atomic weight of the metal (monatomic) at 46·4. Marignac (Ann. Ch. Phys. [3] xxvii. 209), by a similar method, obtained a somewhat higher number, viz. 47·04. Holzmann (J pr. Chem. lxxv. 321), from the mean of his analyses of the sulphate and of the iodate, obtained the number 46·4; and R. Hermann (*ibid.* lxxxii. 385), from his analyses of the carbonate, sulphate, and chloride, obtained 46·44. Mosander's determination may, therefore, be regarded as fully confirmed.

LANTHANUM, FLUORIDE OF. Sulphate of lanthanum forms, with fluoride of sodium, a white flocculent precipitate, sparingly soluble in hydrochloric acid. (Hermann.)

LANTHANUM, OXIDES OF. Lanthanum forms two oxides, viz. a *protoxide*, La^2O or $LlaO$, and a *peroxide*, the composition of which has not perhaps been exactly ascertained.

The protoxide is obtained by igniting the hydrate, carbonate, or oxalate, first in contact with the air, afterwards in contact with the reducing gases of the flame. It then forms white lumps having the same texture as the peroxide, and a specific gravity of 5·94. When exposed to the air, it takes up water and carbonic acid, and in contact with water is converted into the hydrate, LaHO, which is a soft white powder resembling slaked lime. By precipitating a salt of lanthanum with potash or soda, the hydrate is obtained as a bulky, translucent precipitate, which rapidly absorbs carbonic acid. Both the hydrate and the anhydrous protoxide dissolve easily in acids, without evolution of gas.

The peroxide, said to have the composition $La^{128}O^{65}$ or $64La^2O.O$, is obtained by igniting the carbonate, oxalate, or nitrate, in contact with the air. It is a light brown or brownish-grey substance, which dissolves in sulphuric, nitric, or acetic acid, with evolution of oxygen, and in hydrochloric acid with evolution of chlorine.

LANTHANUM, OXYCHLORIDE OF, $La^6Cl^2O^2$ or $Lla^4Cl^2O^2 = LlaCl^2.3LlaO$, remains on heating the hydrated chloride (p. 469), and after washing with water, forms a white powder, insoluble in water, but dissolving slowly in hydrochloric or nitric acid.

LANTHANUM, OXYGEN-SALTS OF. The solutions obtained by dissolving either of the oxides of lanthanum in acids, are colourless and have an astringent taste. Most salts of lanthanum are soluble in water; but the carbonate, borate, and phosphate are insoluble. Lanthanum has a great tendency to form basic salts, by precipitation with ammonia for example. Many of these salts, the basic nitrate and chloride (oxychloride) for instance, run through the filter as milky liquids during washing. If the precipitate be boiled, the whole runs immediately through the filter; but if it be left in the moist state for a few days, it is converted into a neutral salt, which dissolves in water, while carbonate of lanthanum remains on the filter. Sulphate of lanthanum resembles the corresponding salts of cerium and didymium, in forming with sulphate of potassium a crystalline double salt, sparingly soluble in pure water, and quite insoluble in water saturated with sulphate of potassium.

LANTHANUM, SULPHIDE OF, La^2S, is obtained by igniting the metal in vapour of sulphide of carbon, as a yellow powder, which is decomposed by water, with evolution of sulphydric acid, and formation of the white hydrate of lanthanum. The sulphide may also be obtained by igniting the oxide in vapour of sulphide of carbon, or by fusing it with sulphide of sodium; but it is then of a fiery yellow colour, and when examined by the microscope, is seen to be made up of fine crystals. (Mosander.)

LAPATHIN. The name given by Buchner and Herberger (Rep. Pharm. xxxviii. 337), to a substance which they obtained in a very impure state from the root of *Rumex obtusifolius* (the officinal *Radix lapathi acuti*): it has since been shown to be identical with chrysophanic acid (i. 958).

LAPIS LAZULI. *Ultramarine. Lasurstein.*—A silicate of sodium, calcium, and aluminium mixed with a sulphur-compound of sodium. It occurs sometimes in rhombic dodecahedrons, with imperfect dodecahedral cleavage, but more commonly massive and compact. Hardness = 5·5. Specific gravity = 2·38 to 2·45. Lustre vitreous. Colour rich Berlin or azure blue. Translucent to opaque. Fracture uneven. Before the blowpipe it fuses to a white glass, and if calcined and reduced to powder, loses its colour, and gelatinises in hydrochloric acid. With borax, it effervesces and forms a colourless glass.

Analyses:—1. From the East: *a.* Klaproth (*Beiträge*, i. 189); *b.* L. Gmelin (Schw. J. xiv. 329); *c.* Varrentrapp (Pogg. Ann. xlix. 515); *d.* Köhler (*Rammelsberg's Mineralchemie*, p. 710); *e.* Schultz (*ibid.*).—2. From Vesuvius: L. Gmelin (*loc. cit.*).—3. From the Andes: *a.* Field (Chem. Soc. Qu. J. iv. 331); *b.* Schultz (*loc. cit.*):—

	1					2	3	
	a	*b*	*c*	*d*	*e*		*a*	*b*
Silica	62·0	49	45·50	45·33	43·26	47·1	66·9	45·70
Chlorine	. .	. .	. .	0·42	. .	. .	. .	. .
Sulphuric anhydride	5·4	2	5·89	3·22	5·67	1·2	. .	4·32
Alumina	20·0	11	31·76	12·33	20·22	18·5	20·0	25·34
Ferric oxide	4·0	4	1·23	2·12	4·20	13·7	0·1	1·30
Lime	6·5	16	3·52	23·56	14·73	5·4	. .	7·48
Magnesia	. .	2	. .	. .	. .	. .	. .	. .
Soda	. .	8	9·09	11·45	8·76	. .	10·1	10·55
Potash	. .		. .	. .	. .	6·4	. .	1·35
Sulphur	. .	trace	0·95	?	3·16	1·0?	2·9	3·96
Water	2·1	trace	0·12	0·35	. .	1·0?	. .	. .
	100·0	92	98·06	98·78	100·00	94·3	100·0	100·00

These analyses show that lapis lazuli is not a mineral of definite constitution, but a mixture, a result which is corroborated by its appearance and physical structure. It is, therefore, useless to attempt the calculation of a formula from the analyses. On examining thin slices of the mineral under the microscope, the blue colouring matter is seen to be distributed amidst a white ground. The composition of artificial ultramarine renders it probable that the colouring matter of the natural mineral is either a polysulphide of sodium, or a compound of the protosulphide with a polythionate of sodium.

Lapis lazuli is usually found in granite or in crystalline lime-stones. It is brought chiefly from China, Siberia, and Bucharia; the specimens often contain scales of mica and pyrites. On the banks of the Indus, it occurs disseminated in a greyish limestone.

The richly coloured varieties are highly esteemed for making costly vases and ornamental furniture; it is also employed in the manufacture of mosaics, and when powdered constitutes the rich and durable pigment called ultramarine (*q.v.*)

LAPIS OLLARIS or *Potstone* is a coarse granular dark-coloured variety of steatite.

LARCH. See Larix.

LARDERELLITE. A borate of ammonium occurring at the lagoons of Tuscany, as a white efflorescence composed of microscopic crystals. It contains, according to Bechi (Sill. Am. J. [2] xvii. 130), 68·55 per cent. boric anhydride, 11·73 oxide of ammonium, and 18·32 water, agreeing nearly with the formula $(NH^4)^2O.4B^2O^3.4H^2O$. It is soluble in water, and the hot solution yields another salt, composed of $(NH^4)^2O.6B^2O^3.9H^2O$.

LARDITE. A variety of talc (*q.v.*); also syn. with Agalmatolite.

LARIX EUROPÆA or *Pinus Larix*. The Larch tree. The young branches of this tree exude a kind of manna, from which Berthelot has obtained a fermentable sugar called melezitose (*q.v.*) The bark contains a peculiar acid, to be described in the next article.

LARIXINIC ACID. $C^{10}H^{10}O^5$. (Stenhouse, Phil. Trans., 1863, p. 53; Proc. Roy. Soc. xi. 405.)—A volatile crystallisable acid contained in the bark of the larch-tree, most abundantly in that of the smaller branches of trees from 20 to 30 years old. It is obtained by exhausting the bark with water at 80°, evaporating the extract to a syrup and distilling in vessels of glass, porcelain, or silver. The acid which passes over crystallises, partly on the inner surface of the receiver, but the greater part is obtained in the crystalline form on evaporating the distillate. The brown-yellow crystals thus obtained are purified by recrystallisation and sublimation.

Sublimed larixinic acid forms crystals resembling those of benzoic acid, often an inch long, and having a brilliant silvery lustre; they are monoclinic and usually occur in twins. The crystals deposited from water are also monoclinic. The acid sublimes at 93°, melts at 153°, often volatilises with vapour of water, has a slightly bitter astringent taste, and smells like camphor or naphthalene. The crystals catch fire readily, and burn with a bright flame, leaving no residue. The acid reddens litmus slightly, dissolves in 87·9 pts. *water* at 60°, more easily in boiling water and in *alcohol*, sparingly in *ether*. *Nitric acid* converts it into oxalic acid. When treated with *hydrochloric acid* and *chlorate of potassium* it does not yield chloranil.

The aqueous solution of larixinic acid is precipitated by *baryta-water*, forming an easily decomposible precipitate which contains 34·9 per cent. baryta. The acid is not precipitated by *lime-water* or *sugar-lime*, or by *lead-*, or *silver-salts*; neither does it reduce the metal from the latter on boiling. *Ferric salts* produce, even in dilute solution of larixinic acid, a characteristic purple-red colour.

Larixinate of potassium forms flat red-brown crystals which become darker on recrystallisation, and are decomposed, even by carbonic acid.

Larixinic acid is not found in the bark of *Abies excelsior*, or *Pinus sylvestris.*

LASIONITE. Syn. with Wavellite.

LASURITE. Blue carbonate of copper (i. 783).

LASYLIC ACID. $C^7H^4O^2$. An acid whose phenyl-ether, $C^{13}H^8O^2 = C^7H^3(C^6H^5)O^2$, is produced, together with hydrochloric acid, by the action of oxychloride of phosphorus in excess on salicylate of sodium. When the temperature rises high, a viscid liquid passes over, which, on standing, deposits tabular crystals of the phenyl-ether, leaving a mother-liquor which smells of hydrate of phenyl. (Kolbe and Lautemann, Ann. Ch. Pharm. cxv. 157.)

LATERITE (from *later*, a brick) is a name applied by Indian geologists to a formation common in Ceylon and India, and consisting of reddish clay, more or less hardened, and enclosing nodules of quartz: the Cingalese call it cabook. True laterite is a hard, dense, almost jasper-like, reddish or brick-red rock, consisting of hardened clay enclosing quartz-crystals. A second variety, which is most common in Ceylon, is softer, may be cut with the knife, but hardens on exposure to the air. A third kind is sedimentary or breccia-like, consisting of quartz-nodules loosely embedded in clay, and has been produced by disintegration of true laterite, which appears to be itself a product of the decomposition of granite or gneiss containing hornblende. (Jahresber. 1853, p. 892.)

LATEX. A juice which circulates through plants by means of a set of vessels called the laticiferous tissue or cinenchyma, and coagulates into a gelatinous substance called cambium, which precedes the formation of cells. The descending juice is, according to Frémy, a mixture of several liquids, some of which contain vegetable secretions, while others serve for the development of vegetable organs. In those parts of the vegetable organism which are in process of development, there exists a kind of juice called by Frémy, the *albuminiferous latex*, which closely resembles the young organs in chemical composition, and forms the material for the production of the cambium. Under favourable circumstances, this juice may be obtained tolerably pure by making a slight incision into the growing tissues just below the epidermis. This juice—which is obtained with essentially the same properties from the leaf-stalks of *Colocasia odora*, and the banana tree, the stems of *Stephanotis* and *Tanghinia*, the roots of the arum, and the parenchyma of the gourd—coagulates completely when heated, or on addition of a trace of nitric or tannic acid. It usually exhibits the alkalinity of serum or of egg-albumin; leaves, when dried up, a residue consisting almost wholly of albumin (in fact it is as rich in albumin as blood-serum or milk), and yields ash consisting mainly of alkaline chlorides and carbonates. (Frémy, Compt. rend. li. 647.)

LATHYRUS ANGUSTIFOLIUS. In the seed of this plant, Reinsch found an uncrystallisable bitter substance, vegetable fibre, starch, legumin, vegetable albumin, gum, salts, a fixed oil, a resinous and a waxy substance.

LATROBITE. Syn. with ANORTHITE.

LAUMONTITE. *Laumonite, Lomonite, Efflorescing zeolite.*—A hydrated silicate of calcium and aluminium, occurring in monoclinic crystals, in which the principal axis, orthodiagonal and clinodiagonal are to one another as 0·516 : 1 : 0·8727, and the inclined axes make an angle of 68° 40′. Angle $\infty P : \infty P = 86° 16'$; $oP . (P\infty) = 151° 9'$. Observed planes $oP . \infty P . (\infty P\infty) . +P . -P . -2P\infty$. Cleavage perfect parallel to $\infty P\infty$, also to ∞P. The mineral occurs also in columnar, radiating, or divergent forms. Hardness = 3·5 to 4. Specific gravity = 2·29 to 2·36. Lustre vitreous, inclining to pearly on the cleavage-faces. Colour white, passing into yellow or grey, sometimes red. Streak uncoloured. Transparent or translucent; becomes opaque, and usually pulverulent on exposure. Fracture scarcely observable, uneven. Not very brittle. Before the blowpipe it intumesces and melts to a frothy mass; forms a transparent bead with borax. It gelatinises with nitric or hydrochloric acid, but is not affected by sulphuric acid.

Analyses: *a.* From Phipsburg, State of Maine (Dufrénoy, Ann. Min. [3] viii. 303.—*b.* From Courmayeur, Savoy (Dufrénoy, *ibid.*).—*c.* From Skye (Connel, Edinb. J. of Sc. 1829, p. 252).—*d.* From Huelgoet, Bretagne (Malaguti and Durocher, Ann. Min. [4] ix. 325).—*e.* Red variety from Upsala (Berlin, Pogg. Ann. lxxviii. 415).—*f.* From Port George, Nova Scotia (How, Sill. Am. J. [2] xxvi. 30).

	SiO^2	Al^4O^3	Fe^4O^3	Ca^2O	H^2O		
a.	51·98	21·12	. .	11·71	15·05	=	99·86
b.	50·38	21·43	. .	11·14	16·15	=	99·10
c.	52·04	21·14	. .	10·62	14·92	=	98·72
d.	52·47	22 56	. .	9·41	15·56	=	100
e.	51·61	19·06	2·96	12·53	14·02	=	100·18
f.	50·43	21·64	. .	12·07	15·26	=	100·40

These analyses lead to the formula $Ca^2O.Al^4O^3.4SiO^2 + 4H^2O$ (requiring 51·63 SiO^2, 21·51 Al^4O^3, 11·78 Ca^2O, 15·08 H^2O), or $Ca(Al^2)''Si^2O^6.2H^2O$, which is reducible to that of a hydrated metasilicate, $R^2SiO^3.H^2O$.

Laumontite occurs in the cavities of amygdaloïd, also in porphyry and syenite, and occasionally with calcspar, in veins traversing clay-slate. Its principal localities are in the Faroe Islands, at Diako in Greenland, at Eule in Bohemia, in clay-slate on the St. Gothard, and in large masses in the Fassa valley; at Hartfield Moss in Renfrewshire, accompanying analcime; in the amygdaloïd rocks of the Kilpatrick Hills near Glasgow; and in several trap-rocks of the Hebrides and the north of Ireland. Fine specimens are found at Peter's Point, Nova Scotia: it is also abundant in many places in the copper-veins of Lake Superior, and in several other localities of North America.

Laumontite is remarkable for the facility with which it gives up its combined water, in consequence of which it is often found opaque and friable. This change may be prevented in cabinet specimens by dipping them in a thin solution of gum-arabic. According to Malaguti and Durocher, it loses 2·26 per cent. water when kept for a month in a vacuum, and 3·65 in the exsiccator over sulphuric acid. In damp air it does not effloresce; and the effloresced mineral, when exposed to such an atmosphere, recovers the water which it has lost.

Sometimes the alteration of laumontite by natural processes goes a step further, and carbonate of calcium is formed. A laumontite from Oberscheld, near Dillenburg, thus altered, contains (dried at 100°), according to Wildenstein (Jahresber. 1850, p. 734),

SiO^2	Al^2O^3	Fe^2O^3	Ca^2O	H^2O	CO^2		
39·12	13·43	2·60	25·18	6·22	13·45	=	100

or, deducting carbonate of calcium:

56·33	19·34	3·73	11·64	8·96	. . .	=	100

It has therefore been converted into a mixture of laumontite containing only half of the original quantity of water, with carbonate of calcium and a small quantity of free silica.

Laumontite likewise occurs more or less altered to orthoclase (C. Bischof, *Rammelsberg's Mineralchemie*, p. 631; Lewinstein, *ibid.* p. 997; Jahresber. 1860, p. 771).

Caporcianite (i. 741) is perhaps an altered laumontite.—*Schneiderite*, a zeolite from the gabbro of Tuscany, and containing, according to Bechi (Sill. Am. J. [2] xiv. 64), 47·79 per cent. silver, 19·98 alumina, 16·76 lime, 11·04 magnesia, 1·62 alkali, and 3·41 water, is, according to Breithaupt, a decomposed laumontite. Berlin regards *edelforsite* (ii. 361), and similar minerals from Fahlun and Martenberg in Sweden, as decomposed laumontites.

LAURELIC ACID. An acid obtained, according to Grosourdi (Jahresber. 1851, p. 562), from the berries of *Laurus nobilis* (p. 477).

LAURIC ACID. $C^{12}H^{24}O^2 = \left.\begin{matrix}C^{12}H^{23}O\\H\end{matrix}\right\}O.$ *Laurostearic acid. Pichuric acid.* (Marsson, Ann. Ch. Pharm. xli. 33.—Sthamer, *ibid.* liii. 393.—Görgey, *ibid.* lxvi. 303.—Heintz, Pogg. Ann. xcii. 429 and 583; J. pr. Chem. lxvi. 1.—A. C. Oudemans, Jun., J. pr. Chem. lxxxi. 356.—Gm. xv. 43.)—This acid, belonging to the series $C^nH^{2n}O^2$, occurs in the fat of the bay-tree, *Laurus nobilis* (Marsson); in the fat of pichurim-beans (Sthamer); also in the volatile oil of these beans (A. Müller, J. pr. Chem. lviii. 469); in small quantity, together with many other acids, in spermaceti (Heintz); in croton-oil (Schlippe, Ann. Ch. Pharm. cv. 14); in the fruit of *Cyclicodaphne sebifera* (Gorkom, Tydschrift af Necrl. Indie, lxxxi. 410); in the so-called Dika bread, the fruit of *Mangifera gabonensis*, together with myristic acid, but unaccompanied by any other acids (Oudemans); in the age or axin of the Mexicans, a salve-like fat obtained from *Coccus Axia* (Hoppe, J. pr. Chem. lxxx. 102); and in cocoa-nut oil (Görgey and Oudemans). It may be formed artificially by heating ethal (cetylic alcohol) with potash-lime to 275°—280° (Heintz, Scharling). According to Heintz, it is produced only from mixed (crude) ethal, inasmuch as this substance contains lethal:

$$C^{12}H^{26}O + KHO = C^{12}H^{23}KO^2 + 2H^2.$$

But, according to Scharling, it is obtained from the ethal itself, $C^{16}H^{34}O$, which, according to him, is decomposed by heating with potash-lime, in such a manner as to yield stearic, palmitic, myristic, lauric, and butyric acids. (Scharling, Ann. Ch. Pharm. xcvi. 236; Heintz, Ann. Ch. Pharm. xcvii. 271.)

Preparation.—1. *From Bay-fat.* Laurostearin from commercial oil of bay (p. 476) is saponified with potash-ley; the soap is separated by common salt, and its hot aqueous solution is decomposed with tartaric acid. The lauric acid then rises to the surface in the form of an oil which solidifies on cooling, and is freed from adhering tartaric acid by repeated fusion with water. (Marsson.)

2. *From Pichurim beans.*—Laurostearin from *Fabæ pichurim maj.* is saponified with potash-ley till a clear soap-jelly is formed; common salt is added, and the white, brittle soda-soap thus produced is dissolved in boiling water, and supersaturated at the boiling heat with hydrochloric acid; lauric acid then rises to the surface as a colourless oil, which on cooling solidifies to a white crystalline mass. It is freed from hydrochloric acid by repeated washing with water, and purified by repeated crystallisation from weak alcohol. (Sthamer.)

3. *From Cocoa-nut oil.*—The oil is saponified with weak potash-ley; the soap

decomposed by dilute sulphuric acid, and the mixture distilled as long as fatty acids pass over, the water being repeatedly poured back. The distillate neutralised with potash, solidifies on evaporation to a gelatinous soap, which is separated by common salt, repeatedly dissolved in potash and again separated with salt, to free it from the fatty acids which can be thus removed, and again decomposed with dilute sulphuric acid. It is then neutralised with ammonia; the solution precipitated by chloride of barium; the liquid strained off; and the barium-salts which remain repeatedly boiled with water. The resulting solutions, as they run from the funnel, immediately deposit loose flocks of laurate of barium, and the liquid, as it cools down, becomes turbid and deposits pulverulent caprate of barium. (Görgey; see also *Prep.* 5.)

4. *From Spermaceti.*—The saponification of this substance yields, besides ethal, considerable quantities of stearic, palmitic, and myristic acids, and smaller quantities of lauric acid.—The solution of 10 lbs. of purified spermaceti in 30 lbs. alcohol is boiled for some time with 4½ lbs. caustic potash previously dissolved in alcohol; the solution precipitated with aqueous chloride of barium, and strained while hot; the still warm residue pressed as strongly as possible in a warmed press, then well moistened with alcohol and again pressed; the alcohol distilled off from the solutions; the residue freed from the whole of the soluble matter by repeated treatment with ether; and the portion insoluble in ether added to the barium-salts previously obtained. In this manner are obtained, on the one hand, crude ethal; on the other, the barium-salts of the fatty acids of spermaceti.

The barium-salts suspended in water are boiled with very dilute hydrochloric acid, till the supernatant oily layer appears perfectly clear; the fatty acids thus obtained are dissolved in alcohol; the solution is left to cool; and the crystals which separate are pressed, first alone, then several times after being moistened with alcohol; whereby a mixture of palmitic and stearic acids is separated, while a portion of these two acids, and the whole of the myristic and lauric acids, remain in solution.

The whole of the mixed alcoholic solutions are heated; a concentrated aqueous solution of acetate of magnesium is added, so as to precipitate about $\frac{1}{20}$ of the quantity of fatty acids present; the precipitate which forms on cooling is separated by filtration; acetate of magnesium added to the filtrate in about the same quantity as before, and the same treatment repeated (the liberated acetic acid being neutralised towards the end with ammonia), till acetate of magnesium no longer forms any precipitate even in presence of excess of ammonia. In this manner a number of magnesium-salts (19) are obtained, from which stearic, palmitic, and myristic acids may be separated by processes to be hereafter described in connection with these acids.

The alcoholic solution, from which everything precipitable by acetate of magnesium in presence of excess of ammonia has been thus removed, still retains lauric acid, together with myristic and oleic acids. It is precipitated with acetate of lead; the precipitate is washed with dilute alcohol, dried, and freed from a small quantity of oleate of lead, by treatment with ether; and the undissolved portion is decomposed by prolonged and repeated boiling with very dilute hydrochloric acid, whereby a mixture of acids melting at 39·7° is separated. By repeatedly crystallising this mixture from alcohol, as long as the separated acid exhibits a rise of melting point, lauric acid is ultimately obtained, melting at 43·6°, and not capable of further decomposition by partial precipitation with acetate of barium, while myristic acid remains in solution. (Heintz.)

5. From spermaceti or other fats containing lauric acid, provided they are free from oleic acid, or this acid has been removed by the process to be described below.—The fat is saponified with alcoholic potash; the fatty acids are separated from the ethal or the glycerin, as above described, and dissolved in 10 pts. of hot alcohol; the solution is left to cool slowly in a cellar; and the fatty acids which crystallise out are separated by filtration and pressure. The mother-liquor is diluted with an equal quantity of boiling alcohol and supersaturated with ammonia; acetate of magnesium is added in excess to remove a certain portion of the fatty acids; the alcohol distilled off from the filtrate; the remaining salts decomposed by boiling with dilute hydrochloric acid; the separated acids re-dissolved in a quantity of hot alcohol sufficient to retain them in solution after cooling; and a concentrated solution of acetate of barium equal to about $\frac{1}{12}$ of the weight of the fatty acids, is repeatedly added, as long as a precipitate is thereby formed on cooling. The precipitates last obtained, which contain chiefly lauric acid, are separately decomposed by boiling dilute hydrochloric acid, and each portion of acid thereby liberated, whose melting point lies above 43·6, is separately and repeatedly crystallised from dilute alcohol, till its melting point has risen to 43·6. (Heintz.)

If the fat contains oleic acid, it is saponified, the fatty acid is separated and mixed with a small quantity of hot alcohol, and the solid portions are removed by submitting the cooled mass to pressure. The mother-liquor (together with the alcohol used for washing the separated acids) is precipitated with ammonia and neutral acetate of lead; the washed and dried lead-salts are completely freed from oleate of lead by means of ether; the undissolved portion is decomposed by boiling hydrochloric acid; and the separated fatty acids are treated as above (Heintz). In this manner, pure lauric acid is easily obtained from cocoa-nut oil (which, according to Oudemans, does not contain oleic acid). If the acids dissolved in alcohol be precipitated in small portions with acetate of barium, the first portions contain palmitic and myristic acids; and from the remaining liquid, lauric acid may be obtained by repeated fractional precipitation, or by crystallisation in the cold. (Oudemans.)

Properties.—Lauric acid solidifies after fusion to a scaly crystalline mass, exhibiting a laminated texture on the fractured surface; from alcohol, in white, silky needles, united in tufts, or in prickly glandular scales. It melts to a colourless oil at 43·6° (Heintz), 42°–43° (Marsson, Görgey), 43° (Sthamer), 45° (Müller), 43·8° (Schlippe), 43·5 (Oudemans). The alcoholic solution has a slight acid reaction. Specific gravity 0·883 at 20° (Görgey). When boiled with water it volatilises with the vapour. (Görgey, Oudemans.)

It is insoluble in *water*, but dissolves easily in *alcohol* and in *ether*.

By the distillation of its calcium-salt, lauric acid is resolved into laurostearone and carbonate of calcium. (Overbeck):

$$2C^{12}H^{24}O^{2} = C^{23}H^{46}O + CO^{2} + H^{2}O.$$

Laurates. Lauric acid is monobasic, the general formula of its salts being $C^{12}H^{23}MO^{2}$.

The *barium-salt*, $C^{12}H^{23}BaO$, is prepared as above described (p. 474), and crystallises on cooling from a boiling saturated aqueous solution in snow-white flakes. The saturated alcoholic solution becomes filled, on cooling, with delicate crystalline spangles, which, after drying at 100°, resemble caprate of barium (Görgey). It is wetted by alcohol and ether, but not by water (Görgey). Dissolves in 10,864 pts. of water at 17·5°, in 1,982 pts. boiling *water*, in 1,468 pts. cold and 211 pts. hot *alcohol* (Görgey). Decomposes before melting. (Heintz.)

The *calcium-salt* is a white precipitate, obtained by mixing the solutions of laurate of sodium and chloride of calcium.

The *lead-salt*, $C^{12}H^{23}PbO^{2}$, forms a snow-white, loose, amorphous powder (Heintz); laminæ, having a beautiful nacreous lustre (Müller). It melts between 110° and 120°, and solidifies to a dull, amorphous mass (Heintz); melts below 100° to a colourless liquid, which solidifies in the crystalline form on cooling (Müller). It is insoluble in *water*; insoluble in cold, sparingly soluble in boiling *alcohol*. (Müller.)

The *copper-salt*, $C^{12}H^{23}CuO^{2}$, is obtained by precipitating the hot alcoholic solution of the aqueous sodium-salt with aqueous sulphate of copper.

The *silver-salt*, $C^{12}H^{23}AgO^{2}$, obtained by precipitating the solution of the sodium-salt in weak alcohol with nitrate of silver, is a white powder, consisting of slender microscopic needles (Heintz). It dissolves easily in ammonia, and crystallises from the hot concentrated solution in very small needles (Marsson). It is scarcely or not at all altered by light, but decomposes before fusion when heated. (Heintz.)

The *sodium-salt*, $C^{12}H^{23}NaO^{2}$, prepared by nearly saturating a boiling solution of pure carbonate of sodium with lauric acid, evaporating over the water-bath, dissolving the remaining soap in alcohol, and evaporating the filtrate to dryness, forms a white powder, whose alcoholic solution solidifies on cooling to a white opaque jelly. The aqueous solution becomes turbid when largely diluted with water.

LAURIC ETHERS. *Laurate of Ethyl*, $C^{12}H^{23}O^{2}.C^{2}H^{5}$, is prepared by passing hydrochloric acid gas into an alcoholic solution of lauric acid, adding water, which separates the ether, washing first with alkaline, then with pure water, and drying over chloride of calcium. It is a colourless oil, having a fruity odour and sickly taste. Specific gravity 0·86 at 20° (Görgey). Crystallises at 10°. Boils at 269°, when the barometer stands at 750 mm. (Delffs); at 264°, with partial decomposition. (Görgey.)

Vapour-density by experiment 8·4; by calculation (2 vol.) = 7·9.

Laurate of Glyceryl, or *Laurostearin*. $C^{27}H^{50}O^{4}$ [or rather, perhaps, $C^{27}H^{52}O^{5}$ $= \left.\begin{matrix}(C^{3}H^{5})''' \\ H.(C^{12}H^{23}O)^{2}\end{matrix}\right\} O^{3}$].—This fatty body is found in the berries of the sweet bay-tree (*Laurus nobilis*) (Marsson); also in cocoa-nut oil (Görgey), and in pichurim beans. (Sthamer.)

Preparation.—1. *From the berries of the Bay-tree.*—These berries are treated with boiling alcohol; the solution is filtered hot; the crystals of impure laurostearin which separate on cooling are melted over the water-bath; the liquid thus obtained is filtered to separate a resinous substance which accompanies it; and the remaining laurostearin is purified by repeated crystallisation from alcohol. It is thus obtained perfectly pure.

2. *From Commercial Oil of Bay.*—The oil is exposed to sunshine on porcelain plates covered with glass shades, whereupon the green colour soon disappears, and brown hard lumps of laurostearin separate from the mass of fat melted by the sun's heat; these are separated by filtration, dissolved in alcohol, and obtained of a pure white by evaporation or by precipitation with water. (Bolley.)

3. *From Pichurim beans* (*Fabæ pichurim major.*).—The beans are exhausted with cold alcohol (which extracts volatile oil, pichurim-camphor, resin, a buttery fat, and a brown colouring matter); and the exhausted beans are boiled with alcohol of 81 per cent., and pressed between hot plates. The expressed liquid, as it cools, deposits pale yellow laurostearin, only a small quantity of that substance remaining dissolved in the alcohol. It is purified by washing with cold alcohol, pressure, and recrystallisation from ether-alcohol. (Sthamer.)

Laurostearin forms white needles having a silky lustre, melting at about 44°, sparingly soluble in cold alcohol, moderately soluble in boiling alcohol, very soluble in ether. By dry distillation, it yields acrolein. When treated with alkalis, it is resolved into glycerin and lauric acid.

Laurostearin gives by analysis 73·19 to 73·53 per cent. carbon, and 11·45 to 11·68 hydrogen, agreeing nearly with the formula $C^{27}H^{50}O^4$ (calc. 73·97 C, 11·41 H, and 14·62 O), according to which, laurostearin contains the elements of 2 at. lauric acid + 1 at. glycerin − 3 at. water:

$$2C^{12}H^{24}O^2 + C^3H^8O^3 - 3H^2O = C^{27}H^{50}O^4.$$

This, however, does not agree with the constitution of the normal glycerides (ii. 878), Perhaps, therefore, the true formula may be $C^{27}H^{52}O^5 = 2C^{12}H^{24}O^2 + C^3H^8O^3 - 2H^2O = \left.\begin{array}{l}(C^3H^5)''' \\ C^{12}H^{23}O)^2 \\ \quad H\end{array}\right\} O^3.$

LAURIN. *Bay-berry Camphor.*—A substance discovered by Bonastre (J. Pharm. x. 32) in the berries of the bay-tree, and further examined by Marsson (Ann. Ch. Pharm. xli. 329) and Delffs (*ibid.* lxxxviii. 354). It is prepared by boiling the skinned and pounded berries with alcohol of 85 to 90 per cent., filtering at the boiling heat, and leaving the liquid to itself for several days. Laurostearin is then first deposited; and on filtering again and leaving the liquid to evaporate, laurin is deposited in crystals contaminated with a viscid oil, from which they may be freed by pressure between paper and recrystallisation.

Laurin forms crystals belonging to the dimetric system, destitute of taste and smell, insoluble in water, very soluble in alcohol, even in the cold—also in ether. The solutions are neutral to test-papers. Laurin does not dissolve in alkalis.

According to the analysis by Delffs, laurin contains 76·5—77·1 per cent. carbon, and 86·92 hydrogen, numbers agreeing approximately with the formula $C^{22}H^{30}O^3$.

Laurin cannot be distilled without decomposition. Its alcoholic solution is not precipitated by acetate of lead or nitrate of silver.

LAURONE. $C^{23}H^{46}O = C^{12}H^{23}O.C^{11}H^{23}$? *Laurostearone.*—A substance produced by the dry distillation of laurate of calcium. It crystallises from alcohol in shining plates, which melt at 66°. It becomes electric by friction. Gives by analysis 81·42 and 81·04 per cent. C, and 13·82—14·10 H, agreeing nearly with the preceding formula (81·65 C, 13·61 H, and 4·74 O), which is that of the acetone of lauric acid. (Overbeck, Pogg. Ann. lxxxvi. 591.)

LAUROSTEARIN. See LAURATE OF GLYCERYL (p. 475).

LAURUS CAMPHORA, OIL OF. See i. 729.

LAURUS NOBILIS. The *Sweet Bay-tree.*—The fruit of this tree has been analysed by Grosourdi (J. Chim. méd. [3] vii. 257, 321, 385; Jahresber. 1851, p. 562). He finds that, in the fresh berries, the pericarp constitutes nearly a third of the entire weight; the kernels, freed from episperm, make up more than half the weight of the seed; and the episperm amounts to rather more than $\frac{1}{11}$th of the weight of the fresh seed.

100 pts. of the dried berries yielded 0·86 silica, 0·12 carbonate of calcium, 0·12 oxides of iron and manganese, 0·53 carbonate of potassium, 0·07 sulphate of potassium, 0·15 chloride potassium: in all, = 1·75 per cent. ash.

The composition of the entire fresh fruit, pericarp and kernel (cotyledons), is given in the following table:—

Composition of Bay-berries.

	Pericarp.	Kernel.	Entire Seed.
Water	47·417	39·539	42·216
Starch	. .	37·827	21·929
Lignin	32·850	7·783	20·526
Oil of kernels	. .	5·975	3·377
Oil from pericarp	4·724	. .	1·560
Stearolaurin	0·210	. .	0·068
Stearolauretin	. .	0·180	0·008
Pectin or Pectic acid	2·772	. .	0·888
Resin	2·054	. .	0·663
Phæosin or Phæosic acid	3·318	5·685	5·341
Laurin	. .	1·428	0·853
Uncrystallisable sugar	4·301	1·003	2·080
Lauretin	. .	0·120	0·009
Lauretic acid	0·650	0·360	0·403
Albuminous matter	0·200	0·110	0·320
Colouring matter	1·619	. .	0·488
Volatile oil	0·005	trace	trace
	100·120	100·010	100·729

Laurelic acid was obtained by treating the pericarp with water, precipitating the pectin with alcohol, evaporating the alcoholic liquid, dissolving the residue in water, precipitating the aqueous solution with nitrate of lead, and decomposing the precipitate with sulphydric acid.

Stearolaurin (? identical with laurostearin) is the solid fat which gradually separates at 10° from the warm-pressed oil of the pericarp.—*Phæosin* or *Phæosic acid* is a brown substance extracted by carbonate of sodium from the pericarp, exhausted successively with water, alcohol, and ether.

LAVA. See VOLCANIC PRODUCTS.

LAVENDER, OIL OF. Lavender (*Lavandula Spica*, L.) yields a yellowish volatile oil, having a strong but agreeable odour, and an acrid aromatic taste. It reddens litmus, and contains, in variable proportions, a crystalline substance having the composition of common camphor (Dumas). The liquid portion of the oil appears to be mainly composed of two substances, one of which has the composition of oil of turpentine. (Gerhardt, *Traité*, iv. 336.)

LAVENDULAN. An amorphous mineral from Annaberg in Saxony, which appears to be an arsenate of cobalt, mixed with the arsenates of nickel and copper. It has a greasy lustre, inclining to vitreous. Hardness = 2·5 to 3. Specific gravity = 3·014. Colour lavender-blue. Streak paler blue. Translucent. Fracture conchoïdal. Melts easily before the blowpipe, colouring the flame blue, and becoming crystalline on cooling. (Breithaupt, J. pr. Chem. x. 505.)

LAZULITE. *Azurite. Azure-stone. Blue Spar. Voraulite. Klaprothin.*—A hydrated phosphate of aluminium, magnesium, and iron, occurring in monoclinic pyramids, with truncated summits and several secondary faces. The inclined axes make an angle of 88° 15′; and the principal axes, orthodiagonal and clinodiagonal, are to one another as 0·86904 : 1 : 1·0260. Angle $\infty P : \infty P = 91° 30'$; $oP : P\infty = 139° 45'$. Observed faces, $+2P\infty$, $-2P\infty$, $-2P$, oP, $+2P$, $-P$, and others. Twin-crystals also occur with face of composition $\infty P\infty$. Cleavage lateral, indistinct. The mineral also occurs massive.

Hardness = 5 to 6. Specific gravity = 3·057 (Fuchs); 3·067 to 3·121 (Prüfer); 3·122 (Smith and Brush). Lustre vitreous. Colour azure-blue, commonly of a fine deep blue when viewed along one axis, and a pale greenish-blue along another.

When heated in a tube, it gives off water and turns white. Before the blowpipe, it colours the flame faint green, swells up, becomes tumid, but does not melt; gives a fine blue colour with cobalt solution.

Analyses.—*a.* Light blue from Krieglach in Styria: mean of two analyses (Rammelsberg, *Mineralchemie*, p. 340).—*b.* Light blue from near Werfen in Saltzburg (Fuchs, Schw. J. xxiv. 373).—*c.* Dark blue from the Fischbach Alp in Styria: mean of two analyses (Rammelsberg, *loc. cit.*).—*d.* Dark blue from Sinclair County, North Carolina (Smith and Brush, Sill. Am. J. [2] xvi. 365).

	P^2O^5	Al^4O^3	Mg^2O	Fe^2O	Ca^2O	H^2O		
a.	44·16	33·14	12·52	1·77	1·53	6·88	=	100
b.	42·70	36·50	9·54	2·70	. .	6·19	=	97·63
c.	42·58	32·89	9·27	8·11	1·11	6·04	=	100
d.	43·76	31·70	10·04	8·17	. .	5·59	=	99·26

From these numbers Rammelsberg deduces the formula, $[3(Mg;Fe)^2O.P^2O^5].3Al^4O^3.P^2O^5 + 3H^2O$. The darker varieties contain a larger proportion of iron than the lighter varieties.

Lazulite occurs in narrow veins traversing clay-slate, in the torrent beds of Schladming and Rädelgraben, near Werfen in Saltzburg, and the other localities above mentioned; also at Tijuco in Minas Geraes, Brazil. It is abundant at Crowder's Mount, Lincoln County, North Carolina. (Dana, li. 405.)

LEAD. Synonyms: *Blei; Plomb; Plumbum; Saturnum.* Symbols and Atomic weights, Pb = 103·5; Ppb = 207.

This metal does not often occur in nature in the metallic state; but of all the instances in which it is recorded to have been found native, the most reliable are those in which it was discovered among volcanic products.

The colour of lead is bluish-grey; and when it is cut, the fresh surface has considerable lustre; but this brilliancy disappears in a short time, in consequence of the formation of a thin crust of suboxide.

The lead of commerce is nearly pure, as shown by the analyses given at p. 504; the impurities, often present in very small quantities, are silver, copper, antimony, and sometimes iron and manganese.

Lead is very soft, is easily cut by a knife, and may be scratched by the nail. It readily receives impressions, and leaves a streak on white paper. It is very malleable and ductile, and is capable of being rolled into thin sheets or drawn into wire. It occupies the sixth rank among metals as to malleability, and the eighth rank as to ductility. Rolled lead is more ductile than cast lead, in the proportion of 7 to 5. Its malleability and ductility are much affected by the presence of impurities, especially by the oxide of lead, which it dissolves in small quantities in the melted state.

It is very deficient in tenacity; a wire $\frac{1}{12}$ of an inch in diameter does not support 20 lbs. In this respect, rolled and cast lead are precisely alike; but with the latter, the fracture takes place at once, and the ends are clean and granular.

Lead begins to melt at 325° C., and is completely fused at 335° C. (635° F.); at a red heat, it gives off vapours. At a temperature of 50° P., it loses ·005 of its weight in a charcoal-lined crucible, which increases to ·09 as the heat rises to 150° P., whereas galena loses 3·71 per cent.

It crystallises in regular octahedrons. Mongez obtained it in four-sided pyramids by slow cooling; and Marx procured it in fern-like forms, similar to those in which sal-ammoniac crystallises, by allowing a considerable quantity of melted lead to cool until half had solidified, then piercing the crust and running off the fluid portion. By the electro-chemical action of zinc in a solution of acetate of lead, it is deposited in an arborescent form, known under the name of *Saturn's Tree.* Landrin states that, in 1826, he noticed, in a deep mine in Cornwall, cubical crystals of lead which had been deposited on the miner's tools, and had been entirely oxidised. The presence of silver interferes with the crystallisation.

Lead emits a dull sound when struck with a hammer; but when cast in the form of a mushroom, it becomes sonorous.

The specific gravity of lead is, according to Kupffer, 11·3305; Brisson and Herapath, 11·352; Morveau, 11·358; Karsten, 11·3888; according to Berzelius, when in a state of purity, 11·445.

Its specific heat, according to Cooke, is 0·031400. It is an inferior conductor of heat and electricity.

Lead is pyrophoric in a state of fine division. It is usually obtained in this state by heating tartrate of lead in a glass tube as long as any fumes are evolved, when the tube is sealed by a blowpipe. On breaking the tube after cooling, and scattering the powder in the air, it will burn with a red flash.

When lead is melted in contact with the air, the surface is rapidly coated with an iridescent pellicle, which then passes into a yellow oxide. When the temperature is high enough to melt the oxide, it is absorbed by the lead, which loses its lustre and ductility: it becomes brittle, and all the faces of the fracture are dull. It recovers all its original properties by refusion with charcoal.

The action of air and water on lead has been carefully studied by Prof. Miller, from whose account of their combined action we give the following particulars:—This metal undergoes no change in a perfectly dry atmosphere, nor when sealed up in contact with pure water from which the air has been expelled by boiling. It is, however, subject to a powerful corrosion when exposed to the combined action of air and *pure* water. The surface of the lead then becomes oxidised, the water dissolves the oxide, and this solution absorbs carbonic acid, when a film of hydrated carbonate of lead, $2PbHO.Pb^2CO^3$, is deposited in silky scales. Another portion of oxide is formed, which is dissolved by the water, and thus a rapid corrosion of the metal ensues. This action is materially modified when various salts exist in the water, even when their quantity does not exceed 3 or 4 grains in the gallon. The corrosion is increased by the presence of chlorides and nitrates, but diminished by sulphates, phosphates, and carbonates, the oxide of lead being scarcely soluble in water containing these salts in solution. Acid carbonate of lime is remarkable for its preservative influence; and in consequence of the presence of this salt in most spring waters, they do not act on lead to any serious extent, a film of carbonate of lead being deposited on the surface of the metal, and protecting it from further action.

The action of *water* on lead is very important in a sanitary point of view, as this metal is so constantly employed in making cisterns, pipes, &c. for domestic purposes. Rain-water from the roofs of houses, especially in towns, is sufficiently impure to prevent its action on the metal. The most insoluble salt of lead is the hydrated oxycarbonate (p. 478) which is only soluble to the extent of about 1 pt. in 4 millions or one-sixtieth of a grain per gallon of water. When a solution of lead is exposed to the air, silky crystals of this hydrated oxycarbonate are formed, and in a few hours the water does not contain more than $\frac{1}{4,000,000}$ of lead in solution. Water, however, which contains much carbonic acid in solution, is very dangerous, as it dissolves the carbonate of lead. When such water is boiled, the carbonic acid escapes, and the carbonate is deposited. Water has generally so much action on lead, that slate cisterns are much safer than those made with lead.

The *non-oxidising acids* do not act upon lead, except when in contact with the air, as already explained in the case of carbonic acid. *Nitric acid* easily acts on lead, even in the cold, forming protoxide, which is then dissolved. Strong *sulphuric acid* converts the lead into sulphate, when the acid is heated to the boiling point. *Hydrochloric acid* has little or no action, but aqua regia converts the lead into chloride. When *arsenic* or *arsenious acid* is heated with lead, arsenite and arsenide of the metal are formed.

Lead is readily oxidised by *cupric oxide*, which is at the same time reduced to the state of cuprous oxide: it also partially reduces the cuprous oxide, but the oxide of lead which is formed retains a portion of the oxide of copper in combination and prevents any further action on the metallic lead.

Nitre acts rapidly on lead at a high temperature, forming a fusible compound of protoxide of lead and potash. The *acid sulphates* also oxidise this metal; but the neutral sulphates and the alkaline carbonates have no action.

Sulphur, *selenium*, *phosphorus*, and *arsenic* combine directly with lead.

Lead also alloys with most of the *metals*; but only imperfectly with copper, titanium, uranium, cerium, cobalt, nickel, and iron.

EXTRACTION OF LEAD.

Historical Notices. The most abundant and valuable ores of lead possess so many properties likely to attract the attention of uncivilised nations, that it is not surprising to find early mention of this metal. Some authorities think that allusion is made to its metallurgy in the Hebrew word *opher*, in reference to the powder produced by the formation of the oxide on molten lead. The earliest mention of lead is in the well-known passage in the Book of Job; and it is again named as one of the spoils taken from the Midianites in the Book of Numbers. It is also probable that galena was used as a glaze for earthenware in the time of Solomon, from the notice in Proverbs xxvi. It was also one of the articles in which the Phœnicians traded, and which they may have obtained, in part at least, from this country. It was used in the hanging gardens of Babylon, the level of each terrace being covered with sheets of solid lead.

The Romans also worked the ores of this metal both in Spain and in this country. In the former country, the extent of the Carthaginian mining and smelting operations excite our surprise in the present day, and the slags left by them have been re-smelted on a large scale within the last twenty years, while lead cast in Roman moulds—*pigs*, in fact, of the age of Hadrian and other emperors—have been found in Flintshire, Yorkshire, and other localities.

The methods of obtaining the lead from its ores have not undergone any great change, the smelters having adopted the reverberatory or blast furnace as they found the one or the other more suited to the character of the ores of each locality. The one great improvement in the metallurgic treatment of this metal is Pattinson's desilverising plan, which has been followed by the softening process for the hard leads of commerce, especially those of Spain; and we may remark that the only other addition to the ancient methods has been the condensation of the lead fume.

The Ores of Lead. Lead is seldom found native, but there are upwards of twenty ores of this metal known to the mineralogist. Those of practical importance, however, are very few in number, and all the lead of commerce may be said to be procured from five minerals, viz. the carbonate, sulphate, phosphate, arsenate, and the sulphide, the latter ore furnishing more of this metal than all the others.

Sulphide of Lead, or *Galena*, is found in the older and more recent strata, and more or less, in every country of the globe. It occurs in veins in the killas of Cornwall, and in the mountain limestones of Derbyshire and the northern counties. In Cardiganshire and Montgomeryshire, it occurs in the strata of the lower Silurian rocks; and the chief deposits of the United States are found in the rocks of the same geological age. It fills veins in gneiss in Saxony; at Sala in Sweden, it is found in granular limestone.

Analyses of Galena.

Locality .	*Lauenstein, Hanover.*	*Przibram, Bohemia.*		*England.*	*Inverkeithing, Scotland.*
Analyst .	Westrumb.	Lerch.		Thomson.	Robertson.
Lead . .	83·00	81·80	83·61	85·13	84·63
Silver . .	0·08				
Iron . .	. .	. .	. .	0·50	
Zinc . .	. .	3·59	2·18		
Sulphur . .	16·41	14·41	14·18	13·02	13·21
	99·49	99·80	99·97	98·65	97·84

Sulphide of lead occurs also, in combination with the sulphides of antimony and copper, in the minerals *Geocronite*, *Boulangerite*, *Jamesonite*, *Bournonite*.

Carbonate of Lead, or *Cerusite*, occurs in crystals, and in fibrous, compact, and earthy masses. It is frequently found in lodes, and sometimes in beds in sedimentary limestone, generally associated with galena. It is worked in quantity near Aix-la-Chapelle, and in the neighbourhood of Santander in Spain. It is also found in the mines of Cornwall and Devonshire, in Yorkshire, at Leadhills in Anglesey, and at Seven-Churches in Wicklow.

Analyses of Cerusite.

Locality . . .	*Leadhills, Scotland.*	*Nertschinsk.*	*Griesberg, in the Eifel.*	*Oberlahnstein, Nassau.*
Analyst . . .	Klaproth.	John.	Bergemann.	Wildenstein.
Oxide of lead . .	82	81·4	83·51	83·64
Oxide of iron . .	. .	. .	. .	. .
Clay	. .	. .	. .	. .
Water	. .	. .	. .	. .
Carbonic acid . .	16	15·5	16·49	16·36
	98	96·9	100·00	100·00

Locality . . .	*Benkhausen, Westphalia.*	*Phœnixville, Pennsylvania.*	*Vannes, France.*	*Teesdale, England.*
Analyst . . .	Schnabel.	Smith.	Berthier.	Phillips.
Oxide of lead . .	83·93	84·76	66·0	83·50
Oxide of iron . .	. .	. .	2·3	
Clay	. .	. .	15·3	
Water	. .	. .	2·2	
Carbonic acid . .	16·07	16·38	13·0	16·50
	100·00	101·14	98·8	100·00

Carbonate of lead is also found, with other salts of lead and copper, in the minerals *Cromfordite*, *Susannite*, *Lavarkite*, *Calcedonite*.

Sulphate of Lead, or *Anglesite*, is found in cavities, but more generally in lodes associated with galena and carbonate of lead. It occurs at Leadhills in Scotland; in Cornwall and Derbyshire; in the Channel Islands; in Spain, Germany, France, and America.

The composition of this mineral is given in the following analyses:

Locality .	*Anglesey.*	*Wanlockhead, Lead Hills.*	*Zellerfeld, Hartz.*
Analyst .	Klaproth.		Stromeyer.
Oxide of lead . .	71·0	70·50	72·46
Oxide of iron. . .	1·0	. .	0·09
Oxide of manganese .	. .	. .	0·06
Water	2·0	2·25	0·51
Sulphuric acid . .	24·8	25·75	26·09
	98·8	98·50	99·21

Sulphate of lead also occurs combined with other salts, in the form of *Linarite*, *Caledonite*, *Leadhillite*.

Phosphate of Lead, or *Pyromorphite*, occurs generally at the upper parts of lodes, less frequently in layers, and also usually associated with other ores of lead. There are three classes of this ore, viz. such as contain only phosphoric acid; secondly, those containing both phosphoric and arsenic acids; and lastly, those containing lime and fluorine.

The composition of some of the ores of the first class, is given in the following Table:

Locality .	*Leadhills.*	*Poullaouen.*	*Kransberg.*	*Beresov.*
Analyst .	Wohler.	Karsten.	Sandberger.	Struve.
Chlorine . .	2·52	2·53	2·67	2·54
Lead . . .	7·39	7·56	7·80	7·40
Oxide of lead . .	74·50	74·15	73·22	73·36
Phosphoric acid .	15·59	15·76	15·94	15·82
Oxides of iron and chromium .	. .	. .	. .	0·59
	100·00	100·00	99·63	99·71

This ore is found at Leadhills, and in Cornwall; at Wicklow in Ireland; at Phœnixville, in the United States; and many other localities.

Arsenate of Lead or *Mimetesite* is met with in large quantities at Drygill, in Cumberland, and has been used in the manufacture of flint glass, to which it imparts great brilliancy. It is found at Redruth and other Cornish mines; at Beeralston in Devonshire, and in America, Siberia, &c., generally occurring near the outcrop of the veins. There are three classes of it, similar to those of the previous ore. The following is the composition of a specimen of the ore which contains arsenic acid, analysed by Bergemann:

	From Blanca, Mexico.
Oxide of lead	74·96
Arsenic acid	23·06
Chlorine	2·44
	100·46

The other ores of lead will be found described in these volumes under their respective mineralogical designations.

Metallurgical Treatment of the Ores of Lead. The differences in the nature of the ores of lead, the peculiarities of the localities as to labour, fuel, &c., and the application of the lead afterwards, have all tended to modify the metallurgy of this valuable metal. It would have been more satisfactory to have described all the different plans in detail; but as this would be inconsistent with the limited space which can be devoted to a metallurgical subject in these volumes, we must confine this article to an account of some of the methods adopted for extracting lead from its ores. Various arrangements might also be pursued in this account of the smelting of lead ores, but we prefer the following, in which we will describe—I. Reduction of the Ores. II. Refining of the Lead. III. Softening of Hard Lead. IV. Smelting of the Slags and other Products. V. Condensation of the Lead Fume.

I. Reduction of Lead Ores.

All the ores of lead may be arranged in two classes in respect to their metallurgical treatment, viz. the sulphur and oxygen compounds of lead, and again as to the form of furnaces employed in their reduction, viz. the reverberatory and the blast furnace.

1. THE REDUCTION OF SULPHUR ORES IN REVERBERATORY FURNACES.

The sulphur ores of lead are treated after two different systems in the reverberatory furnace, which have been distinguished by Phillips as the *method of double decomposition* and the *process by affinity*, and these again differ in the details as practised in this country, in France, and in Germany.

The first plan depends upon the reaction between sulphide of lead and oxide of lead, as shown in the following equation:

$$\mathrm{PpbS} + 2\mathrm{PpbO} = 3\mathrm{Ppb} + \mathrm{SO}^2$$

or upon the double decomposition when sulphide and sulphate of lead are the constituents of the mixture, thus:

$$\mathrm{PpbS} + \mathrm{PpbSO}^4 = 2\mathrm{Ppb} + 2\mathrm{SO}^2.$$

This process consists in roasting the galena in a reverberatory furnace, until a portion of the ore has been converted into oxide and sulphate of lead; it may be performed either in a distinct furnace, or in the smelting furnace where the subsequent fusion is effected. The following table of analyses of roasted ores, from different localities, illustrates the above remarks.

Analyses of Roasted Galena.

Locality .	*Pezey.*	*Holzapfel.*		*Pontgibaud.*		
Oxide of lead . .	18	35	31·0	52·6	16·9	62·9
Sulphate of lead . .	86	19	8·0	8·0	12·1	
Sulphide of lead . .	10	4	11·8			
Oxide of iron . .	. .	6	9·0	13·0	21·3	4·9
„ zinc . .	. .	27	30·2	9·0	21·6	3·7
„ manganese .	. .	2				
„ antimony .	.					
„ copper . .						
Arsenic acid . .	. .	. .	. .	0·4	1·0	
Sulphate of baryta .	. .	. .	. .	14·0	19·8	0·7
Silica	. .	7	10·0	3·0	6·2	23·9
Lime, &c. . . .	. .	. .	. .	. .	. .	3·1
	114	100	100·0	100·0	98·9	99·2

When the roasted ore has been thoroughly mixed, the doors are closed and the fires are set away. The reactions above explained then take place, when the lead is separated.

This process is applicable to the ores which are comparatively free from silica and earthy impurities, and is generally adopted in England.

The process by affinity consists in fusing the ore with iron in some form or other, when, the iron combining with the sulphur, the lead is eliminated: thus,

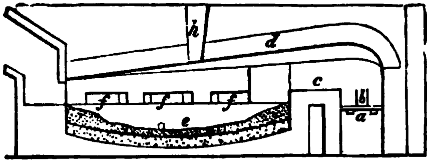
$$\mathrm{PpbS} + \mathrm{Ffe} = \mathrm{Ppb} + \mathrm{FfeS};$$

and this plan is better suited to the impure ores of lead.

a. *Method by double Decomposition.*

ENGLISH PROCESS.—*The Reverberatory Furnace* consists, as usual, of three essential parts, the fireplace, hearth and chimney. The position and relative proportions of each part are shown in *figs.* 589 and 590, where *a* represents the grate; *b*, the door of the fireplace; *c*, the fire-bridge; *d*, the arched roof; *e*, the hearth; *ff*, the working doors; *g g*, flues running into one main flue leading to a condensing-chamber and chimney.

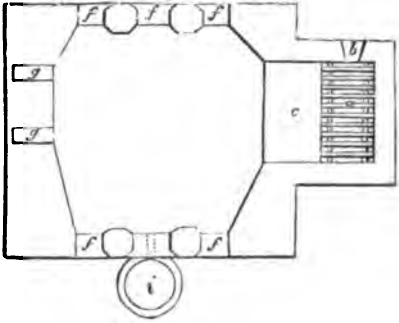
Fig. 589.



The hearth is hollow or funnel-shaped, to facilitate the descent of the lead to the lowest point in the bed of the furnace. The bottom of these furnaces, or hearth, as it is called, is built of bricks, which are covered with a layer of slags. These slags are run into a semi-fluid condition by a heavy fire, and then worked into the proper shape by means of paddles and rakes. The hearth slopes more rapidly from the fire-bridge than from the flue, to prevent the lead being exposed too long to the action of the heated air.

There are three working doors on each side of the furnace, attended by two men, who assist each other in manipulating the charge. The lead collects at the lowest part of the hearth, covered by the slags, and is drawn off by a *tap-hole* into the metal pot, *i*, in front of the furnace.

Fig. 590.



The arch falls rather rapidly towards the flues, *g g*, to give more effect to the heat, and the draught is capable of regulation by means of dampers.

The usual charge of ore in these furnaces at Holywell weighs 20 cwt., which is introduced through a hopper, *h*, in the arch of the furnace. This charge is then spread evenly over the surface of the earth, and gently heated for two hours, the doors being closed and the damper lowered.

The two front doors, farthest from the fire, being opened, the smelter throws in the slags swimming on the surface of the lead in the pot, *i*, from the previous operation. The tap-hole is opened in a little time to allow the metallic lead to run off from the slags, and at the same time, an assistant turns over the ore, through the back doors, by means of a paddle. These doors are now closed, while the front ones are open, through which some small coal is thrown in upon the lead-bath, and the whole is worked up together, the ore being turned over with a paddle. The smelter, in about three-quarters of an hour from the commencement, throws back upon the sole of the hearth, the fresh slags, which then float upon the bath, and are mixed with the coaly matter. These slags and the ore are then turned over with the paddle, and all the doors are closed.

The ore is turned over again through the back doors, and the first lead appears, obtained from the slag last remelted. This lead is run off by the tap, and both workmen then turn over the ore, through all the doors. The smelter now closes all the front doors except that next the fire-bridge, and lifts off the fresh slags from the lead pot, drains them, and throws them back into the furnace. The interior of the furnace, at this period, has a dull red heat.

The lead begins to separate from the ore in about 1½ hour from the charging of the furnace, and the two workmen again turn over the ore from each side of the furnace. Some coal is thrown on the grates, slightly to raise the heat, the ore is turned over, and all the doors are closed.

The *first fire* or roasting lasts about two hours, and the damper is then raised a little; coal is thrown on the grates to give the *second fire*, which lasts 25 minutes. The heat of the furnace has now become bright red, and the lead flows from all sides to the bath. The smelter then pushes the slags back towards the upper part of the hearth, while the assistant spreads them over its surface, through the back doors. The smelter now throws in a few shovelfuls of quicklime upon the lead-bath, through the middle door. The assistant works the ore and slags through the three back doors, spreading them out, while the smelter again pushes the slags from the inner bath to the upper part of the sole. The doors are left open for a short time, and the lead flows down into the basin from the slags with which it was mixed as they were pushed back.

The workmen in a short time again turn over the ore and slags, and in three hours from the commencement, a little more fuel is thrown on the grate. In ten minutes, fresh fuel is added for the *third fire*, the damper is fully raised, all the doors are again closed, and the furnace is left in this state for three-quarters of an hour. At the expiration of about four hours, all the doors being opened, the assistant levels the surface to facilitate the separation of any lead, and then spreads the slags which are pushed back towards him by the smelter, who now throws in more lime to render the slags less fluid and to cover the lead-bath.

The smelter adds a fresh charge of fuel in about ten minutes after the completion of the third fire, and closes the doors to give the *fourth fire*. This fire is finished in four hours and forty minutes, when the doors are opened, the tap-hole is pierced to allow the lead to flow into the pot outside, and some lime is thrown upon the slags in the inner bath. The smelter then pushes these *dried* slags towards the upper part of the hearth, whence the assistant rakes them out of the furnace through the back doors.

We have given this detailed account of the working of a charge from Mr. Phillips' excellent description of the process followed in Wales, as an illustration of the nature of these operations, and to avoid the necessity of similar minute details in other analogous processes.

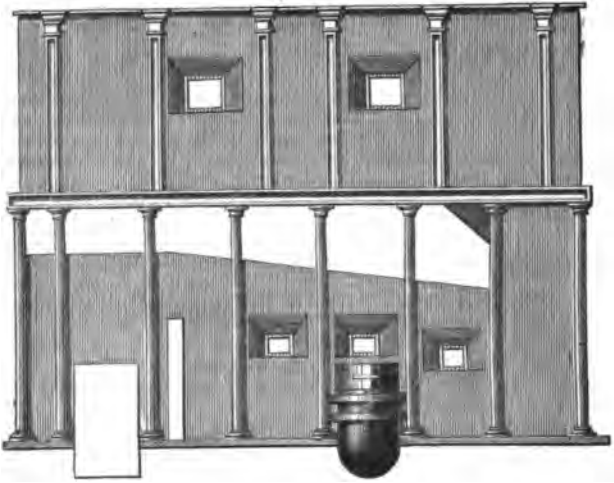
The weight of a charge varies in different localities, 12 to 14 cwt. being that used in the north of England; 21 cwt. in Bristol, and 30 cwt. in Cornwall, while the time extends from 6 to 24 hours, according to the weight and nature of the ore.

The cost of smelting an average parcel of galena in the reverberatory furnace is:

	s.	*d.*	
Labour	9	7·2	per ton of ore.
Coals 19·9 cwt. . . .	3	3·8	„
Lime 0·9	0	4·9	„
Repairs	0	4·0	„
	13	7·9	

In some smelting works, the roasting process is conducted in a distinct furnace, and in other mills, the two furnaces are combined in the manner shown in *fig.* 591, which represents the front or tapping side of the furnace. It is unnecessary to give any details of this form, after the description of the previous furnace.

Fig. 591.



When the process of roasting is conducted in a separate furnace, as a distinct operation, the cost per ton, from an average of upwards of 700 tons, is as follows:

	s.	*d.*
Labour	3	2·5
Coals 5·6 cwt. . . .	0	11·2
Repairs	0	1·8
	4	3·5

This is probably the most suitable place to notice the results of some experiments made by Plattner and other chemists, on the loss of silver which occurs during the roasting of ores containing this metal, and which we can confirm from our own experience.

1. The loss of silver arises from chemical reactions.
2. The volatilisation of the silver appears to take place at the moment when it passes into the metallic state from its combination with sulphur, or when the sulphate of silver is decomposed.
3. The loss of this metal increases with the duration of the roasting, and the rise in the temperature.
4. The loss also increases when the oxides of iron or copper are present to decompose the sulphate of silver.
5. The loss is not so great with the silver-compounds of arsenic and antimonic acids, obviously because these salts are not so soon decomposed as the sulphate of silver.

We may also here notice the proposal of Fallizé, to tap the lead at different periods, instead of doing so at the end of the operation. He founds his proposal on the fact, that the lead which is first reduced, is the richest in silver; and by keeping the different products distinct, the subsequent operation of desilverising would be to some extent anticipated as well as facilitated, by providing leads varying in their richness in silver.

We believe this suggestion to be well worthy of adoption, as we have found the lead obtained in smelting rich ores to fall from 74 oz. to 44 oz. silver per ton, according to the period when the lead was collected.

Another proposal for treating galena containing silver has also been made. The galena is to be mixed with 1 per cent. of chloride of lead, and 10 per cent. of common salt, and the mixture fused, when it is said the galena will be desilverised, and the chloride of silver will float on the surface with the common salt. The mixture of the latter salts is then to be reduced, with any chloride of lead that may be present. We have great doubts as to the economical results of this process, having found the loss of lead to be most serious, whenever any chloride of lead was present.

Carinthia Process.—The furnace employed in this process differs from the English, as indicated by *figs.* 562, 563.

Fig. 592 represents a front elevation, and *fig.* 593 a horizontal section. Two furnaces are built side by side, and work into one chimney. The hearth of these furnaces is narrow, sloping regularly from the fire-bridge to the flue; and is so arranged that the fluid contents will flow to the metal pot *a*, outside the furnace. The hearth is formed of two concentric beds, the lower one of beaten clay, and the upper of fused slags. The arch is curved like the sole, but in an opposite direction, and at its highest point, is 23 inches above the hearth. The fireplace is shown by the dotted lines *ppp*, and the products of combustion, passing over the hearth, escape to the chimney *h*, through a flue over the working door. In recent furnaces of this form, the hearths are constructed one above the other, the operation being completed in the lower hearth.

Fig. 592.

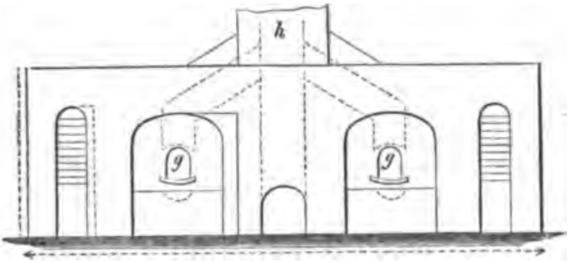
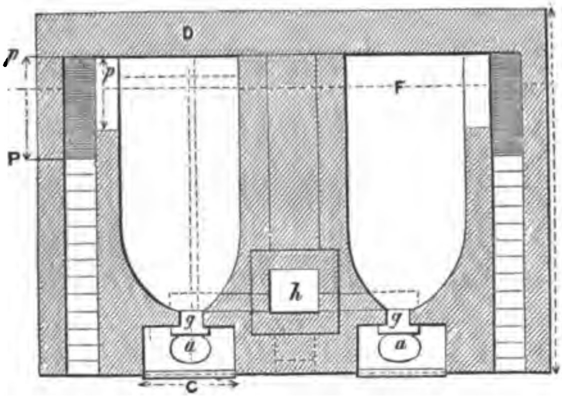


Fig. 593.



The fuel employed consists of the wood of the spruce and pine, and the charge of ore weighs about 420 lbs. The working lasts 23 hours, and the produce is very large. The slags, when rich in lead, are washed and treated again. The lead flows into the outer pot, is purified by a second fusion, and then cast into pigs.

Kerl has given the following explanation of the reactions on which this Carinthia process is founded.

When galena is roasted at a low but gradually increasing heat, a portion of the sulphide is converted into sulphate of lead, along with some oxide of lead, while part of the sulphide remains unchanged.

When the temperature is raised, during the vigorous stirring of the ore, a quantity of lead is liberated, as already explained. Some subsulphide of lead is, however, also formed, which likewise reacts with the sulphate of lead, producing metallic lead; thus,

$$Ppb^2S + PpbSO^4 = 3Ppb + 2SO^2.$$

During this first period of the operation, lead is continuously liberated, and runs down to the bath in the hearth. The progress of the roasting converts more and more of the sulphide into sulphate of lead, diminishing the liberation of lead until a point is reached, when oxide of lead is the only product of the reaction; thus,

$$PpbS + 3PpbSO^4 = 4PpbO + 4SO^2.$$

The second stage of the operation is then in progress, when, by the addition of red-hot charcoal and an increased temperature, the litharge is reduced and another portion of lead is obtained.

French Process.—When galena is exposed to a continuous and slowly increasing temperature, a large proportion is converted into sulphate of lead, and a smaller portion into oxide of lead. If the roasting is interrupted at this point and the heat raised, but not so high as to induce fusion, these compounds react upon each other, producing oxide of lead, which furnishes metallic lead by the reducing action of coal; thus,

$$\begin{aligned} PpbS + 3PpbSO^4 &= 4PpbO + 4SO^2 \\ PpbO + C &= Ppb + CO. \end{aligned}$$

The coal also reduces the sulphate of lead ultimately into metallic lead and sulphurous acid. At a low heat, only half of the sulphate is converted into sulphide of lead; thus,

$$2PpbSO^4 + C^2 = PpbSO^4 + PpbS + 2CO^2.$$

And as the temperature is raised, the same reaction occurs, as explained in the Carinthia process.

Fig. 594.

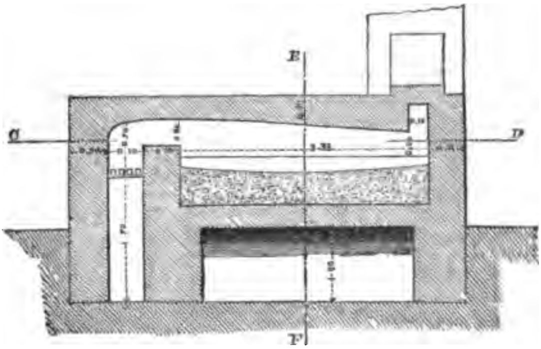
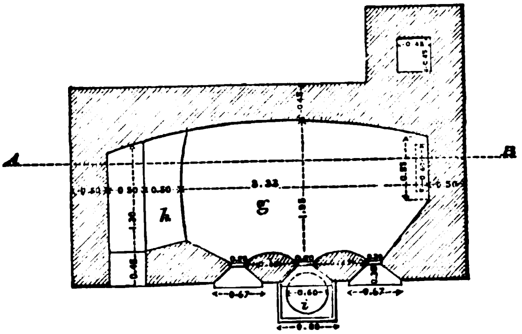


Fig. 595.

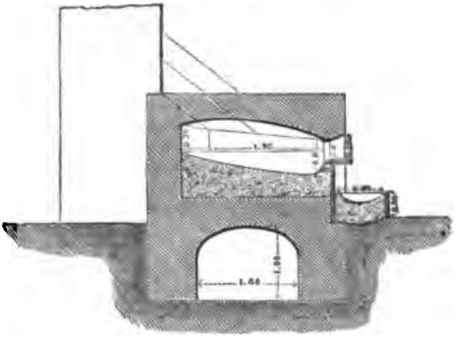


The French process is founded on these reactions, and the furnace employed is represented by *figs.* 594, 595, 596, the first being a longitudinal, the second a horizontal, and the third a transverse section.

There are three doors close together on the same side, and in front of the middle door the lead pot *i* is built. The firebridge *h* is 23 inches wide, and the hearth *g*, 11 feet by 6½ feet. The hearth is made with a tenacious clay resting upon an arch of granite.

A charge of ore weighs 2600lbs.; it is heated so gradually that at the end of five hours a dark red heat is reached. The doors are closed, and the heat raised till the ore commences to soften. The smelter now vigorously works the ore, when the reactions above explained take place, and the lead runs into the metal pot *i*. A second roasting for two hours follows, and then another turning over of the contents of the furnace. This alternate roasting and working is repeated several times, and at the end of 13 hours, some coal and wood are thrown into the furnace, to reduce the oxide of lead. A last roasting and stirring are then given, and the slags withdrawn from the furnace.

Fig. 596.



The composition of the slags obtained in the preceding processes is given in the following table:

Analyses of Lead-slags from Reverberatory Furnaces.

	Pezey.	Holz-apfel.	Poullaouen.			Bir-ming-ham.	Katz-enthal.	Gras-sing-ton.	Lea, near Matlock.			
Silica . . .	17·0	10·0	24·0	29·5	35·6	29·4	27·6					
Oxide of lead . .	13·0	38·9	26·5	2·5	·4	15·6	11·0	34·0				
Protoxide of iron .	53·5	5·6	14·0	64·5	42·0	13·4	26·2	3·0	4·5	2·0	15·4	5·6
Oxide of zinc . .	. .	30·5	27·0	1·0	20·8	. .	3·4	. .		2·0	7·2	8·0
Oxide of manganese	. .	2·0	. .	. .	. .	. .	4·6					
Baryta . . .	11·5											
Lime . . .	. .	. .	. .	. .	. .	28·4	. .	. .	8·0	8·0	16·0	14·7
Alumina . . .	. .	. .	. .	2·5	1·0	5·7	1·6					
Sulphide of lead .	5·0	5·0	5·0	. .	. .	5·5	4·0	. .	. .	. .	17·0	2·0
Sulphate of lead .	. .	8·0	3·0	. .	. .	. .	. .	. .	22·0	9·0	12·0	30·0
Sulphate of calcium.	. .	. .	. .	. .	. .	. .	. .	10·5	22·5	33·0	1·6	5·6
Sulphate of barium .	. .	. .	. .	. .	. .	. .	. .	51·0	25·0	30·0	22·0	24·4
Fluoride of calcium	. .	. .	. .	. .	. .	. .	. .	1·5	16·0	13·6	7·2	8·5
Phosphoric acid .	. .	. .	. .	. .	. .	. .	15·0					
Carbon . . .	. .	. .	. .	. .	. .	. .	4·6					
	100·0	100·0	99·5	100·0	99·8	98·0	98·0	100·0	98·0	97·6	98·4	98·7

The lead is purified by stirring it with beams of wood and repeated skimmings, after which it is refined.

Action of the Gangue.—All the ores of lead contain more or less of other earthy and metallic compounds, which exercise a considerable influence on the chemical reactions which the smelter aims at accomplishing. When these foreign bodies are present in a large proportion, the processes just described are not adapted for the treatment of such ores, which are smelted by other methods to be hereafter explained. It will, however, be useful to take a rapid survey of the influence which these gangues exert on these processes.

Carbonate of Calcium.—When this substance is present in small quantities, it facilitates the chemical action, by contributing to the decomposition of the sulphide of lead, with formation of sulphate of calcium, and by preventing the materials becoming too fluid at the moment when the most important reactions are taking place. It has been found that 10 to 12 per cent. of this substance may be present in the ore without being prejudicial.

Sulphate of Barium.—This substance remains perfectly inert during the whole operation of smelting, and is objectionable therefore only as a mechanical hindrance, by diminishing the contact of the compounds of lead which are to act on each other in the furnace. Galenas which contain 15 per cent. of this gangue are, on this account, unfitted for treatment in the reverberatory furnace.

Fluor Spar.—This mineral is very similar in its action to the carbonate of calcium, but it is very beneficial when present with sulphate of barium, towards which substance it acts the part of a flux.

Quartz, Clay, and Silicates.—These gangues, when present only to the extent of 5 or 6 per cent., are very injurious, and it is impossible to obtain any lead in the reverberatory furnace, when they amount to 12 per cent. During the roasting they are inert, but when the heat reaches a dark red, and before the sulphide and oxide of lead react on each other, the silica unites with the latter, forming very fusible basic silicates, rendering the whole charge fluid, and preventing any further action.

Blende.—This ore may be present to the extent of 10 or even 15 per cent. without much prejudice to the working in the reverberatory furnace. It does not complicate the treatment, and is objectionable only by its conversion into oxide and sulphate of zinc, which are inert, and prevent the intimate mixture of the lead-compounds. The small portion of blende which escapes oxidation during the roasting, reacts afterwards on the oxide of lead, producing sulphurous acid, oxide of zinc, and metallic lead. When coal is introduced in the subsequent operations, the oxide of zinc is reduced at the same time as the oxide of lead, and the zinc, being very volatile, carries off a considerable portion of lead.

Iron Pyrites.—The presence of a small quantity of this mineral does not seriously interfere with the smelting operations. During the roasting, the pyrites is more rapidly oxidised than the galena, and what escapes, afterwards assists in reducing the oxide of lead. In the concluding operations, the oxide of iron is disseminated through the mass, and retards the fusion of the lead-compounds. A large proportion of pyrites is, however, very prejudicial, as that portion which is unoxidised, forms a very fusible matt with the sulphide of lead, which escapes the reduction.

When the pyrites is arsenical, the lead is always rendered more or less impure by the presence of arsenic, which increases the loss of both lead and silver in the subsequent cupellation.

Sulphide of Antimony.—This ore is always very injurious, even when present only to the extent of 2 or 3 per cent. It gives rise to the same reactions as galena; and, a portion of the antimony being brought to the metallic state, combines with the lead, rendering the latter hard, and occasioning a loss of both lead and silver when submitted to cupellation. The compounds of antimony also form very fusible compounds with those of lead, which cannot then be brought to the metallic state. The great volatility of antimony, its oxide and sulphide, also increases the loss of lead and silver.

Copper Pyrites.—This mineral renders the ores unfit for treatment in the reverberatory furnace. Even when it is present in such small quantities as not to interfere with the reactions, the lead always retains a portion of the copper, which diminishes its commercial value.

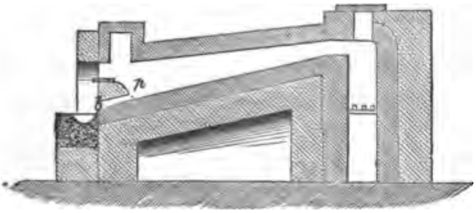
Carbonate of Iron.—This substance acts only as a mechanical hindrance in the furnace, where it is gradually converted into oxide of iron. During the later period of the operations, it retards the fusion of the slags, and postpones the reactions until nearly all the sulphide of lead is oxidised. This gangue therefore, when present in small quantities, is favourable rather than otherwise in the reverberatory furnace.

b. *Process by Affinity.*

This plan was used in France for treating a Spanish galena which contained a large proportion of quartz, and is founded on the reactions already explained.

The furnace employed is shown in *fig.* 597, and is charged with about 800 lbs. of ore through a side door. This charge is mixed with 200 to 240 lbs. of iron, which ought to be in the form of scrap iron, as cast iron, mill cinder, and iron ores are not found to answer equally well with malleable iron. The mixed charge is then rapidly heated until the galena begins to soften, when the temperature is kept stationary to permit the reactions to take place. The lead, as it is reduced, flows to the lower part of the furnace at *p*, while the matt swims on the surface, and this again is covered by the slag. The contents are then drawn off through the tap-hole *b*, into the metal pot.

Fig. 597.



A modification of this plan has been proposed by Phillips and Rivot, who employ a furnace with a hearth slightly inclined towards a basin at the side, placed before one of the two side doors.

The furnace is to be charged with 1600 lbs. of ore, which must be carefully spread over the hearth, and roasted for 12 hours at a moderate heat. At this point, if the ore does not contain sufficient silica, 12 per cent of sand and 1½ per cent. of charcoal are added. The heat is rapidly brought up to a cherry-red, when the charcoal reduces the oxide of lead, and facilitates the action of the sand, which decomposes the sulphate, forming silicate of lead. The charge passes through a process of boiling, and when this subsides, a quantity of iron is thrown in while the charge is being well worked; the iron decomposes the silicate of lead, producing metallic lead and silicate of iron. When the slags are properly impoverished, the contents of the furnace are tapped into the pot, where the lead remains, and the slags flow off at one side.

Mr. W. J. Cookson has introduced another modification of this principle. He mixes the lead ore and iron together, and adds a small quantity of alkali and carbonaceous matter. This mixture is exposed to heat in large crucibles, when a very pure lead is obtained. The matt falls to powder, which is afterwards mixed with a little water, made into bricks, and burnt in kilns, as a substitute for sulphur ores, in the manufacture of sulphuric acid.

The Reduction of Oxygen-ores of Lead.

Carbonate of Lead.—When this ore of lead contains a large proportion of galena, it is treated by one of the plans already described, but when tolerably pure, it is submitted to special operations.

The furnace is of the ordinary reverberatory character, in which the hearth has only a slight inclination towards the tap-hole at one of the sides. The ore, in the form of a fine sand, is mixed with some reducing agent, such as coal, and some flux adapted to the nature of the gangue. This charge is then spread upon the hearth, the doors are closed, and the heat is gradually raised, during which the mixture is often turned over. The temperature is kept as low as possible, and the lead, gradually reduced, falls down to the tap-hole, through which it is drawn off from time to time.

When the lead has ceased to appear, the spongy mass on the hearth, is heated until it fuses, when the whole is drawn out and smelted in a blast furnace.

Sulphate of Lead.—This salt of lead is found native, and large quantities are also produced in various chemical and other manufactories. In the latter case, it is often mixed with an excess of sulphuric acid, which must be expelled in a reverberatory or other furnace.

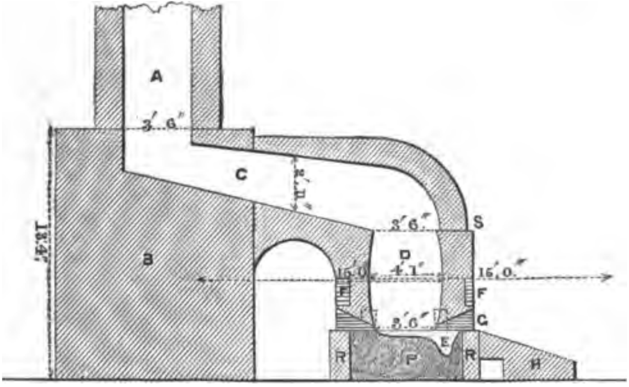
The only mode of treating this compound of lead is that proposed by Phillips and Rivot, to which we must refer the reader.

Spanish Air-furnace, or *Horno de gran tiro.*

This furnace, shown in *figs.* 598—600, does not differ from the blast furnace in its form, but as the draught depends entirely upon the chimney, it may be said, in this respect, to resemble the reverberatory furnace, and finds its appropriate position in this part of the article.

Its height is 8 feet, and the diameter varies from 3½ feet to 4 feet. The charging door, D, is placed a little above the spring of the arch, S. The sole of the furnace, P, is formed of a very refractory material called *Laguena*, a species of decomposed argillaceous slate, which is found in great abundance near Cartagena. It is ground to fine powder, and mixed with coke also in powder, in the proportion of 3 to 1. This mixture is moistened with water, and carefully beaten with rammers. The walls, R, are also

Fig. 598.



built of the slate in its undecomposed state, called *Laja*. The hearth or crucible is then cut out to the shape shown in *fig.* 598. Six openings (*figs.* 599, 600) G G, are left in the walls for the admission of the air, and for drawing off the slags. The flue, C, connecting the furnace and chimney, is carried by an arch, K, and is built so as to be independent of the furnace. The chimney, A, is about 44 feet high, has a large area, and works two furnaces. The air-holes are 15 inches by 12 inches at the outside, and taper to 9 inches by 4 inches next the interior. They are formed by working some clay upon a wooden mandril, and placed to point towards the centre of the furnace. There are also other holes (register), F, above the air-holes, but temporarily built up, so as to be easily opened when required. An inclined plane, H, is built to draw away the slag, as in an iron blast furnace, and it is kept cool by an air-channel below. The lead is collected in a small pot, T, through an opening cut through the sole to the hearth.

Fig. 599.

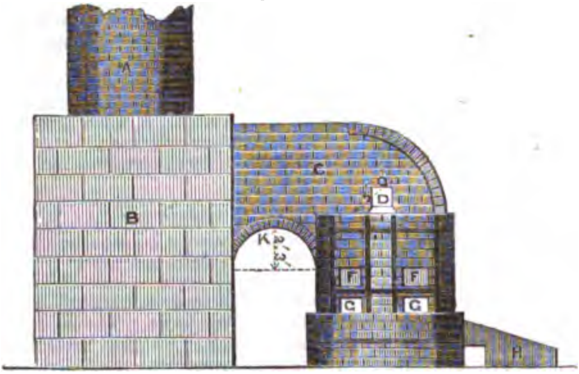
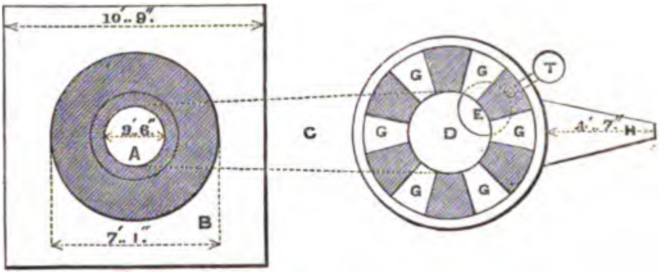


Fig. 600.



The ore smelted in these furnaces contains carbonate of lead and galena, mixed with oxide and carbonate of iron, oxide of antimony, carbonate of lime, clay and sands. This ore is used raw, mixed with lead-slags, and coke is the fuel employed.

The furnace having been annealed for some hours, 3 or 4 pigs of lead are placed in the hearth to form a bed for the slags, and the furnace is charged with coke. In 5 or 6 hours, a few baskets of slags are thrown in with a little granulated iron. After a little time, the slags begin to run down the incline, when the regular charge of ore is added. The air-holes are regularly watched to keep them all at the same degree of heat, as any neglect is apt to allow the materials to harden, when these air-tuyeres become choked. It is in fact the duty of one man to remove all the *niggers* or hard black lumps, which tend to form in and near them. The furnace is charged only once every hour, as the opening of the charging door, D, injures the draught.

The charge consists of:

40	baskets of ore, or about 5 cwt.	
8 to 10	„	old Slag.
4 to 5	„	coke, with some dry wood.

The latter assists in diffusing the air uniformly through the materials. The quantities used in 24 hours are:

Ore	cwt.	134	Coke	cwt.	20
Slag	„	44	Wood	„	2

As the air has a tendency to ascend round the sides of the furnace, the smelter throws his charges against the walls, and keeps the air-channels as far as possible open to the centre of the furnace. When the furnace becomes *gobbed* in any part, one or more of the register-holes are opened to enable the smelter to remove the obstruction.

The lead is tapped every six hours, and the matt is returned to the furnace. The produce varies from 6 to 7 cwt. of lead upwards, according to the richness of the ore.

We have described this furnace at some length, as it is cheaply built, lasts about 6 to 8 weeks, and can be used in localities where more perfect plans would be impracticable.

2. THE REDUCTION OF LEAD ORES IN BLAST FURNACES.

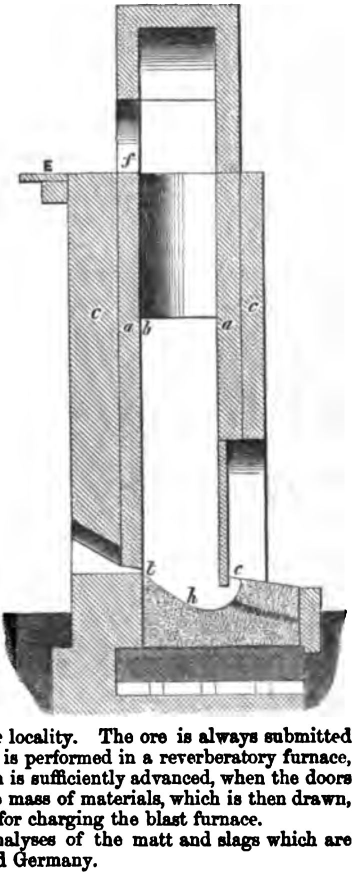
The ores generally smelted in blast furnaces are such as, from the proportion of their impurities, are not adapted to the reverberatory furnace; but this remark does not apply to the peculiar form of blast furnace known under the name of the ore-hearth, as used in America and this country (p. 497).

a. *The Cupola or Blast Furnace.*

This form of furnace is very generally adopted on the Continent, and exhibits at different works a great variety of form and dimensions. The great difference in the ores, the fluxes available and the nature of the fuel, are all so many conditions which require special modifications to overcome the difficulties peculiar to each locality.

We will select, as illustrations of this mode of smelting, three of the modifications in which the ore is used in the raw and roasted form, and in both states.

Fig. 601.



Silesian Furnace.—The form and construction of this furnace are represented in *fig.* 601. The walls, *a a*, are vertical from the tuyere upward; for a distance of 10 feet 4 inches to 6 feet, the section of the furnace is rectangular, while above this point it takes a circular form. The exterior wall, *c c*, is built of common bricks, and the lining or *shirt*, *a*, is constructed of fire-bricks. The charge of raw ore and flux is mixed on the floor, E, and thrown into the furnace through the opening *f*. The blast enters at *t*, and fusion takes place, during which the hearth, *h*, is gradually filled with the lead produced. The slag floats on the surface of the lead, and is drawn off at *c*, while the lead is occasionally tapped through a canal which passes to the bottom of the hearth. The fume is carried away from the top of the furnace through a series of condensing chambers. These furnaces can only be worked for about eight days, when the operation is stopped to repair the lining.

The *lit de fusion* consists of:

Galena in small pieces . .	100 parts.
Cast iron	12 „
Slag from iron forge . .	14 „

Each ton of this charge requires a ton of coal, which is thrown against the front, and the ore, &c. against the back of the furnace.

When the slag contains 7 or 8 per cent. of lead it is resmelted. The matt or regulus, consisting of sulphide of iron and lead, with a little silver, is roasted and smelted in the same furnace.

Hartz Furnace.—This plan is adopted in the Hartz, France, and Belgium, more or less modified according to the circumstances of the locality. The ore is always submitted to previous roasting; and when this operation is performed in a reverberatory furnace, the heat is gradually raised, until the oxidation is sufficiently advanced, when the doors are closed. The fire is then urged to melt the mass of materials, which is then drawn, allowed to cool, and broken up into pieces fit for charging the blast furnace.

The following tables contain numerous analyses of the matt and slags which are obtained from the blast furnaces of France and Germany.

TABLE I.—*Analyses of Matts.*

a. From the Ordinary Process of Smelting Roasted Ores.

Locality .	Freiberg.		Muldner.	Hals-brücke.	Antons-hütte.	Oker.	Pontgibaud.		Pezey.	Villefort.	Poullaouen.		Holzapfel.		Emser.
Authority .	Lampadius.		Plattner.	Ihle.	Kersten.	Ulrich.	Rivot.	Berthier.							
Lead . . .	15·2	25·130	21·816	24·80	9·8	8·64	79·5	5·0	91·5	51·6	85·5	3·5	62·0	49·0	19·0
Iron . . .	1·5	33·120	37·202	15·20	44·0	44·34	12·2	54·6	1·5	24·5	0·9	64·0	2·2	3·3	26·0
Copper. . .	2·1	12·100	12·944	36·20	27·8	17·43	. .	. .	. .	3·0	3·2	0·8	18·6	27·0	17·0
Silver . . .	0·1	0·201	0·099	0·16	{ 1·7 + zinc										
Nickel . . .	35·5	. .	0·544	{ 2·64 and zinc	4·4										
Cobalt . . .	12·4														
Zinc . . .	. .	. .	1·439	. .	. .	7·76	1·1	. .	. .	1·0	. .	. .	trace	2·3	
Bismuth . .	18·7														
Arsenic . .	10·3	2·450	0·731	. .	1·1	. .	{ + anty 4·2	16·8							
Sulphur . .	3·0	19·526	22·847	21·00	11·2	19·64	2·3	23·6	5·0	16·6	10·4	31·6	17·2	18·4	27·5
Antimony . .	. .	4·753	0·718	. .	. .	2·19	. .	. .	. .	1·7	. .	. .	. .	. .	10·5
Earths . . .	. .	. .	. .	. .	. .	. .	. .	. .	2·0	0·6					
	98·8	97·280	98·340	100·00	100·0	100·00	99·3	100·0	100·0	99·0	100·0	99·9	100·0	100·0	100·0

TABLE II.—*Analyses of Matts.*

b. From the Treatment of the Unroasted Ores with Iron.

Locality .	All from the Upper Hartz.													
Lead . . .	73·346	63·0	41·50	13·65	8·26	52·27	36·0	59·33	53·31	65·78	60·69	63·787	35·68	61·71
Iron . . .	9·814	19·0	34·05	63·14	58·00	28·32	33·2	19·60	21·56	13·03	20·36	13·721	31·55	17·91
Copper . .	0·396	0·2	0·36	0·88	0·90	1·42	trace	1·10	0·23	1·15	0·49	1·533	3·79	0·77
Zinc . . .	0·198	. .	. .	. .	. .	1·56	2·5	0·17	2·24	0·67	0·55	2·253	. .	1·30
Antimony . .	0·397	. .	0·66	0·13	2·40	0·31	5·3	0·13	0·38	0·18	0·36	. .	1·49	
Silver . . .	0·116	. .	0·12	0·03	0·02									
Sulphur . .	15·338	17·5	23·82	22·01	31·38	16·12	22·0	18·92	19·33	17·27	16·40	18·706	23·97	18·13
Manganese . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0·25	0·18
Arsenic . .														
Carbon . .	trace													
	99·605	99·7	100·51	99·84	100·96	100·00	99·0	99·25	97·05	98·08	98·85	100·000	96·73	100·00

TABLE III.—*Analyses of Lead-slags from Blast Furnaces.*

a. From Unroasted Ores.

Locality . .	Clausthal.					Altenau.	Lautenthal.	Andreasberg.		Clausthal.					Bleiberg, in Karinthia
Authority . .	Bodemann.			Rammelsberg.	Ulrich.			Kast.		Bodemann.					Plattner.
Silicic acid . . .	48·80	53·9	43·13	45·00	47·57	53·82	41·00	34·82	30·04	53·14	58·10	59·86	57·98	54·48	5·26
Alumina . . .	4·62	4·4	4·76	4·62	3·21	3·82	2·55	9·77	7·96	2·20	3·70	2·51	2·59	6·60	1·76
Lime	3·26	5·6	5·77	6·31	5·26	5·37	6·82	11·72	15·93	5·67	11·03	10·22	10·38	16·16	8·86
Protoxide of iron . .	36·00	32·0	37·72	35·83	32·28	25·90	33·73	24·61	22·66	33·01	21·27	21·22	25·94	19·42	
Protoxide of manganese	. .		0·30	. .	1·35	2·74	1·26	. .	. .	. .	0·80	0·65			
Magnesia . . .	1·24	1·3	0·78	0·75	0·58	1 09	0·62	1·21	0·97	0·33	1·15	0·62	0·18	1·71	1·42
Oxide of lead . .	5·30	4·2	6·32	7·80	3·98	4·79	7·25	12·31	14·13	4·31	2·06	1·68	2·46	1·62	37·71
Teroxide of antimony .	. .	. .	. .	0·50	0·22	. .	. .	0·21	0·27						
Protosulphide of iron .	. .	. .	. .	. .	1·71	3·16	1·58								
Sulphide of zinc . .	. .	. .	. .	. .	1·50	. .	3·60								
Oxide of zinc . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	19·20
Sulphuric acid . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	5·04
Baryta . . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	traces	1·09	0·94	traces		
Molybdic acid . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0·46
Protoxide of copper .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	traces
Suboxide of copper .	. .	. .	. .	. .	. .	. .	. .	0·33	0·34						
Potash . . .	. .	. .	. .	. .	. .	. .	. .	2·34	3·80	. .	. .	. .	.	. .	traces
Soda	. .	. .	. .	. .	. .	. .	. .	0·54	0·68	. .	. .	. .	. .	. .	traces
Arsenious acid . .	. .	. .	. .	.	. .	. .	. .	0·26	0·30						
Sesquioxide of iron .	. .	. .	. .	.	. .	. .	. .	. .	. .	. .	. .	. .	. .	.	19·50
	99·22	101·4	98·78	100·81	97·66	100·69	98·41	98·12	97·08	98·66	99·20	97·70	99·53	99·99	99·21

Analyses of Lead-slags from Blast Furnaces.

(*b.*) From Roasted Ores.

Locality . . .	Freiberg.							Sala (Sweden).	Oker, Unter-harz.	Pontgibaud.
Authority . .	Lampadius.	Merbach.	Kersten.	Erdmann.	Amburger.	Lampadius.		Bredberg.	G. Ulrich.	Rivot.
Silicic acid	28·54	28·00	30·50	37·30	43·26	30·7	28·5	39 39	27·66	39·0
Alumina	5·40	4·50	5·10	8·15	. .	3·7	5·4	6·23	6·00	1·5
Sesquioxide of iron . .	. .	. .	. .	. .	5·62					
Protoxide of iron . . .	46·10	49·89	55·74	40·92	46·95	45·0	46·1	17·18	50·30	21·2
Protoxide of manganese .	. .	. .	2·20	. .	. .	. .	. .	. .	traces	
Lime	8·31	. .	. .	2·66	. .	5·3	8·3	17·77	7·72	11·0
Baryta	1·00	. .	. .	. .	. .	1·0	1·0	. .	. .	26·0
Magnesia	traces	2·00	. .	3·00	0·45	. .	. .	19 13	1·90	2·1
Oxide of lead	4·12	6·05	4·00	7·17	2·00	6·3	4·1	. .	2 13	18·2
Oxide of zinc	3·00	. .	0·85	. .	1·91	4·0	3·1	. .	3·50	1·7
Protoxide of copper . .	traces	6·74	. .	. .	0·25	. .	. .	. .	traces	
Sulphuric acid . . .	2·43	2·25	. .	. .	. .	1·0	2·5	. .	. .	1·0
Sulphur	1·00	. .	. .	. .	1·26	. .	. .	. .	2·23	
Protosulphide of iron . .										
Phosphoric acid . . .										
	99 90	99·43	98·39	99·20	101·70	99·0	99·0	99·70	101·44	121·7

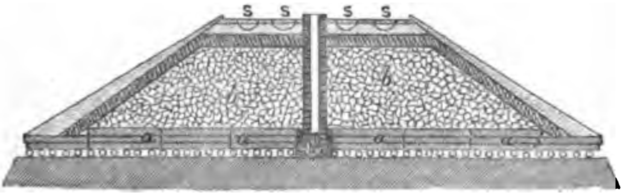
Analyses of Lead-slags from Blast Furnaces—continued.

(*b.*) From Roasted Ores.

Locality	Pontgibaud.			Pezey. Savoy.	Ems.	Holz-apfel.	Ville-fort.	Katz-enthal.	Schemnitz, Hungary.
Authority . . .	Rivot.		Berthier.						Wehrle.
Silicic acid	40·0	38·0	27·0	48·8	23·2	25·0	40·5	29·8	28·5
Alumina	1·7	1·4	7·6	14·0	3·4	1·3	3·8	1·4	6·0
Sesquioxide of iron									
Protoxide of iron	18·7	19·2	32·0	10·0	34·8	21·5	27·0	59·4	34·5
Protoxide of manganese . . .	. .	. .	. .	. .	7·0	8·0	. .	3·6	
Lime	15·0	24·1	13·0	15·3	6·6	4·2	11 7		
Baryta	3·2	3·3	. .	1·0	. .	. .	7·6	. .	5·60
Magnesia	3·2	2·9	. .	. .	0·6	1·0	. .	. .	1·30
Oxide of lead	13·1	6·0	18·6	9·3	2·0	2·0	8·8	traces	17·7
Oxide of zinc	1·5	1·6	. .	. .	6·8	29·0	. .	. .	4 4
Protoxide of copper	. .	. .	. .	. .	2·4	1·0	. .	. .	1·2
Sulphuric acid	2·3	2·1							
Sulphur									
Protosulphide of iron	. .	. .	. .	. .	12·0	4·0	. .	. .	4·80
Phosphoric acid	. .	. .	. .	. .	. .	. .	. .	0·8	
	98·7	98·6	98·2	98·4	98·8	100·0	99·4	95·0	104·0

The ore is sometimes roasted in the open air, as at Rammelsberg, on the Hartz, and Fahlun in Sweden. The ore at the former place, consisting of an intimate mixture of the sulphides of lead, copper, iron and zinc, is formed into heaps, as seen in *fig.* 602.

Fig. 602.

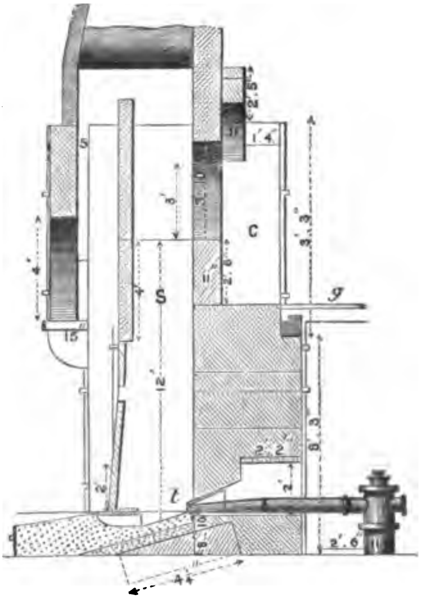


A thick layer of pine wood, *a a a*, is laid down for a foundation, upon which the ore, *b b*, is placed in pieces decreasing in size towards the top. The whole is covered with a layer of roasted ore in powder, which shuts off the access of an excess of air. These heaps contain about 150 tons of ore, and after they are ignited, the combustion is supported by the sulphides, through a period varying from 18 to 24 weeks.

At the top of the pile are a number of cavities, *s s s*, formed in the porous covering, in which a portion of sulphur collects, as it is sublimed from below, and from which it is ladled at times. A ton of sulphur is usually obtained from a heap, and it is said nearly to pay the cost of roasting. The metallic products are afterwards roasted in a second and third heap.

This roasted ore is smelted in a furnace constructed as shown in *fig.* 603. The charge is prepared on the floor, *g*, and thrown into the furnace, s, through the opening c, along with the fuel. A strong blast is driven in through the tuyere, *t*.

Fig. 603.



The charge consists of

Roasted ore	35	cwt.
Highly siliceous slags	10	„
Oxide of lead and pieces old cupels .	¼–½	„

The matt is repeatedly roasted and resmelted to obtain any copper, lead and silver, it may contain.

Spanish Economic Furnace. The discovery of enormous deposits of slags left by the Romans, near Cartagena and other places in Spain, together with the mining of a poor lead ore in these districts, has led, within the last 15 or 20 years, to a very great development of lead smelting on this coast. Furnaces of different descriptions were tried, one after another, but they have all given place to what is known under the above name.

This furnace, as improved by the writer, is represented in *figs.* 604, 605, 606, in elevation, section and plan. The blast enters through three water-tuyeres, *a a a*, and the materials are maintained up to the level of the charging door, *b*. The upper layers are kept cool by a fine rain of water from a rose, *c*, and the steam which is formed assists in condensing the fumes which escape into the flue, through an opening, *d*, in the back side of the top of the furnace. The upper part of the furnace rests upon four metal pillars, *f f f f*, so that when the body of the furnace requires to be renewed, this part remains untouched. The lead accumulates in the hearth, *g*, whence it is tapped, from time to time, into the pot, *h*, to be ladled into moulds. The slag runs continuously into a tank, *i*, which is kept supplied with a stream of water. The slag in this case falls into a coarse sand, which is easily carted away, but it is sometimes run into small waggons, forming large blocks on cooling.

The furnace is circular, with a diameter of from 2¼ to 2½ feet, and built of firebricks moulded to suit the form of the furnace. The body of the furnace is only one brick thick, and when any portion of the wall gives way, the hole is filled with clay, which is driven into the interior, while the smelter lays fresh bricks to rebuild the wall.

The bottom of the furnace is formed in Spain of a kind of clay which is found to answer remarkably well, but in this country a mixture of pure ground coke and fire-clay is employed. This mixture, made into a paste, is very carefully beaten down, and then the hearth is cut out, as shown in the figure (605). The formation of this bottom requires the greatest care, as the duration of the furnace depends more upon its stability than upon the continuance of the walls, which, as already explained, can be repaired from the outside.

Fig. 604.

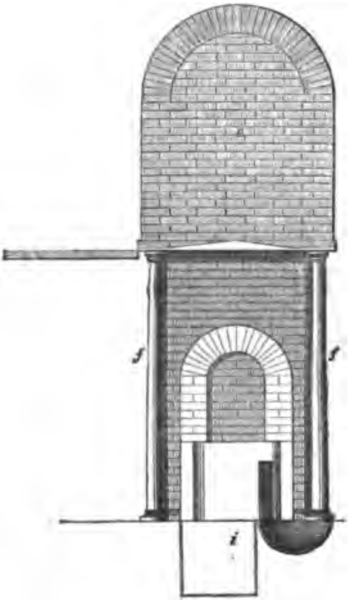


Fig. 605.

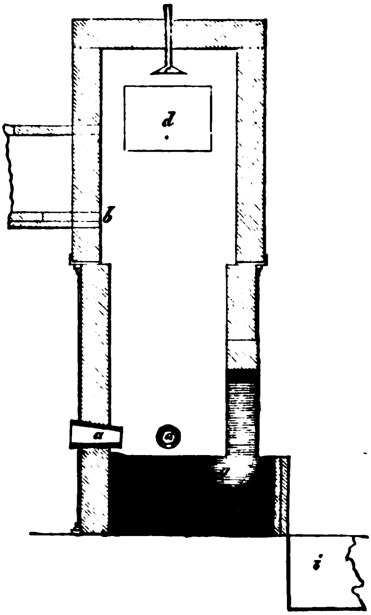
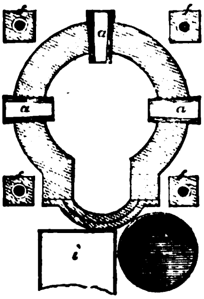


Fig. 606.



The breast of the furnace is made of a semicircular plate of cast iron, with a lip to carry off the slag, and a slit through which the taphole is drilled. Above the breast-pan is an arch about 18 inches wide and 24 in height.

The materials are charged, layer upon layer, of ore and flux and coke. The ore may be either raw or roasted, and the nature of the flux depends upon the character of the gangue. In Spain the ore is sometimes roasted in kilns, consisting of large chambers, something like our fire-brick kilns. The ores or materials containing lead to be smelted in this furnace should not hold more than 20 or 30 per cent. of lead.

When this form of furnace was introduced into this country, the writer made a great number of experiments as to the ores and fluxes which could be most profitably smelted by it; but it would be impossible to give the details in so limited an article as the present. It may, however, possess some interest to give the materials smelted and the cost of one of the first campaigns, which term is employed to designate the time the furnace works without being rebuilt. This campaign lasted 15 weeks, working night and day, and the following weights of ores were smelted:

Spanish ore . . .	3249·50 cwt.	English lead ore slags .	1521·25 cwt.
English lead ores . .	8634·60 „	Litharge	30·50 „
American silver ores .	86·75 „	Litharge cinders . .	973·75 „
			14496·35

There was a gain of silver on the assays, but a loss of lead of about one-tenth on the assays, which, however, it is proper to say, were made most carefully by the best methods. The cost was as follows:

	cwt.	£	s.	d.	£	s.	d.		per ton. s.	d.
1. Wages connected with the furnace					£124	1	9	=	3	5·1
2. Engine power: wages		£10	10	1						
1509 cwt. coals		12	11	6	23	1	7	=	0	7·5
3. Fluxes, Fluor spar	228½	9	15	0						
Carbonate of baryta	14	1	2	6						
Chalk	209½	0	16	2						
Limestone	250	3	13	0						
Rock-salt	144½	6	11	8						
Kelp	5	0	10	0						
Hematite ore	25	0	18	9						
Metal borings	790	79	15	0						
Mill cinder	4673	40	18	3						
Grey slags	704	1	15	9						
Pitch	5	0	1	3						
Coal	19	0	3	2	= 146	0	6	=	4	0·3
4. Fuel—Coke	2667				47	16	1	=	1	3·8
5. Repairs					33	1	0	=	0	10·9
					£374	0	11	=	10	3·6

The following statement contains the cost of smelting the Roman slags near Cartagena, in Spain, calculated on the produce of lead:

Cost of 20 cwt. of Lead.

360 quintals at 8 per cent. lead, washed up to 24 per cent. = 120 quintals for smelting	360 reals
30 „ of coal for engine, at 6 reals	180 „
50 „ of coke for smelting, at 11 reals	550 „
2 smelters, at 8 reals	16 „
4 labourers, at 6 reals	24 „
Wear and tear	50 „
Management, &c. &c.	100 „
	1280 reals

and this expense, at 92 reals per £ sterling, brings the cost of a ton of lead up to £13 6*s.* 8*d.* per ton, where the Roman slags are obtained free of charge.

We believe this form of furnace is admirably adapted for many of our poorer ores and materials containing lead, and that it well deserves the attention of our smelters.

b. *The Ore-hearth.*

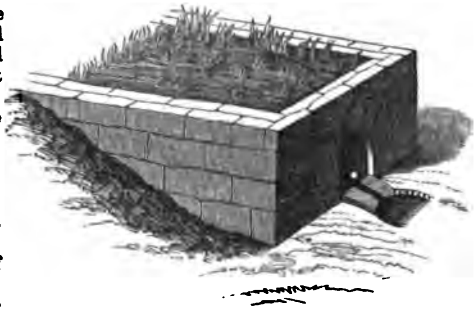
This method of reducing can only be applied to the purest description of ores, and the advantage which it possesses over the reverberatory furnace, consists chiefly in the greater purity of the lead which is produced. This, however, is of great commercial importance, as such lead is suitable for conversion into the best white and red leads, and in consequence brings £1 per ton more in the market than ordinary soft lead. The ore hearth is also worked with less consumption of fuel and a smaller outlay in labour. The cost of the furnace is much less and the working may be discontinued and resumed at any time without repairs being required.

The first construction to be noticed is that of

The Backwoods Hearth.

This form of furnace is of the most primitive character, and yet the practice of the Western backwoodsman is still more simple; if he wants shot or bullets, he kindles a fire in a hollow tree, or an old stump of a tree, places some galena on the charred wood, and melts it down, when after cooling, he finds the metal at the bottom of the hollow.

Fig. 607.



In Missouri, the ore was reduced in square furnaces, constructed of logs or stones, as shown in *fig.* 607.

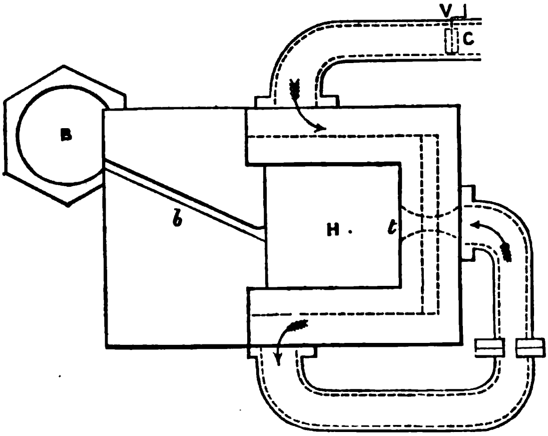
The air is admitted through the arch in the fore-side, and the lead is collected in the basin in front. The management consists in placing a layer of heavy logs at the bottom; then billets of split wood are set upright, on which the galena is thrown, the top of the ore being covered with small wood. A fire is kindled in the front arch, which chars the lower portion of the wood, and the process of reduction commences. The lead runs into the basin, and the operation lasts 24 hours. The ashes are collected after the furnace cools, and they are smelted in what is called an *ash-furnace.*

This plan is now superseded by constructions of a modern type.

The American Hearth.

This furnace (*fig.* 608) is sometimes made of cast iron, and so arranged that a hollow case surrounds the hearth, H, through which the air passes on its way to the tuyere, by which contrivance the blast is raised to a high temperature. The air enters through the pipe, C, and, following the course of the arrows, is driven through the tuyere into the hearth.

Fig. 608.



As the ore is reduced, the lead flows down the channel, *b*, into the pot, B. The force of the blast can be regulated by the valve, V.

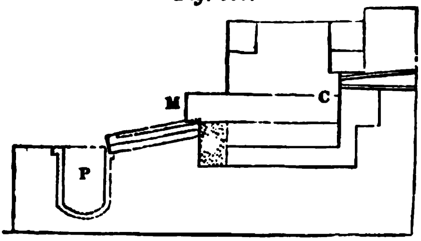
The hearth is first carefully warmed by a wood fire, when the reservoir in the hearth, H, is filled with lead, which soon melts, and upon which the charge floats during the operation. The smelter places several pieces of wood before the blast, and then charges with raw galena. The whole soon becomes heated, the reduction follows, and the lead flows off into B. The first charge is followed by another, and thus the process is continued as long as the smelter wishes.

At Rossie, in New York, 75 cwt. of lead is obtained in 24 hours, and the cost of working is about seven shillings per ton.

The Scotch Hearth

is in use in the northern counties of this country, and Mr. Phillips' account of the mode of working it, is so admirable that we cannot do better then quote it.

Fig. 609.



This furnace (*fig.* 609) is from 22 to 24 inches in height, and 12 to 18 inches area inside, but its horizontal section, always rectangular, varies much in its dimensions at different levels.

The ore can be worked either in a raw or roasted state, but the latter is now generally used, as it yields a better produce, and works dry, allowing the blast to diffuse itself more perfectly through the mass.

In proceeding to smelt by means of an ore-hearth, two workmen are required to be in attendance from the beginning to the end of each smelting shift, the duration of which is from 12 to 15 hours. The first step in commencing a smelting shift is to fill up the hearth-bottom and space below the workstone with peats, placing one already kindled before the nozzle of the bellows. The powerful blast very soon sets the whole in a blaze, and by the addition of small quantities of coal at intervals, a body of fire is obtained, filling the hearth. Roasted ore is now put upon the surface of the fire, between the forestone and pipestone, which immediately becomes red-hot and reduced, the lead from it sinking down and collecting in the hearth-bottom. Other portions of ore, of from 10 or 12 lbs. each, are introduced from time to time, and the contents of the hearth are stirred and kept open, being occasionally drawn out and examined upon the workstone, until the hearth-bottom becomes full of lead. The hearth may now be considered in its regular working state, having a mass of heated fuel, mixed with partly fused and semi-reduced ore, called *browse*, floating upon a stratum of melted lead. The smelting shift is then regularly proceeded with by the two workmen, as follows:—The fire being made up, a stratum of ore is spread upon the horizontal surface of the browse, and the whole suffered to remain exposed to the blast for about five minutes. At the end of that time, one man plunges a poker into the fluid lead in the hearth-bottom below the browse, and raises the whole up at different places, so as to loosen and open the browse, and in doing so, to pull a part of it forwards upon the workstone, allowing the recently added ore to sink down into the body of the hearth. The poker is now exchanged for a shovel, with a head 6 inches square, with which the browse is examined upon the workstone, and any lumps that may have been too much fused, are broken to pieces; those which are so far agglutinated by the heat as to be quite hard, and further known by their brightness, are picked out, and thrown aside, to be afterwards smelted in the slag hearth. They are called "grey slags." A little slaked lime in powder is then spread upon the browse, which has been drawn forward upon the workstone, if it exhibit a pasty appearance; and a portion of coal is added to the hearth, if necessary, which the workman knows by experience. In the meantime, his fellow-workman, or shoulder-fellow, clears the opening through which the blast passes into the hearth, with a shovel, and places a peat immediately above it, which he holds in its proper situation, until it is fixed, by the return of all the browse from the workstone into the hearth. The fire is made up again into the shape before described; a stratum of fresh ore spread upon the peat; and the operation of stirring, breaking the lumps upon the workstone, and picking out the hard slags repeated, after the expiration of a few minutes, exactly in the same manner. At every stirring a fresh peat is put above the nozzle of the bellows, which divides the blast and causes it to be distributed all over the hearth; and as it burns away into light ashes, an opening is left for the blast to issue freely into the body of the browse. The soft and porous nature of dried peat renders it very suitable for this purpose; but in some instances, where a deficiency of peats has occurred, blocks of wood of the same size have been used with little disadvantage. As the smelting proceeds, the reduced lead, filtering down through all parts of the browse into the hearth-bottom, flows through the channel, out of which it is laded into the pig-moulds.

The principal particulars to be attended to in managing an ore-hearth properly during the smelting shift are these: First:—it is very important to employ a proper blast, which should be carefully regulated, so as to be neither too weak nor too powerful. Too weak a blast would not excite the requisite heat to reduce the ore, and one too powerful has the effect of fusing the contents of the hearth into slags. In this particular, no certain rules can be given; for the same blast is not suitable for every variety of ore. Soft, free-grained galena, of great specific gravity, being very fusible, and easily reduced, requires a moderate blast; while the harder and lighter varieties, many of which contain more or less iron, and are often found rich in silver, require a blast considerably stronger. In all cases, it is most essential that the blast should be no more than sufficient to reduce the ore, after every other necessary precaution is taken in working the hearth. Secondly:—The blast should be as much divided as possible, and made to pass through every part of the browse. Thirdly:—The hearth should be vigorously stirred at due intervals, and part of its contents exposed upon the workstone, when the partially fused lumps should be well broken to pieces, and those which are farther vitrified, so as to form slags, carefully picked out. This breaking to pieces, and exposure of the hottest part of the browse upon the workstone, has a most beneficial effect in promoting its reduction into lead; for the atmospheric air immediately acts upon it, and, in that heated state, the sulphur is readily consumed, or converted into sulphurous acid, leaving the lead in its metallic state; hence it is that the reduced lead always flows most abundantly out of the hearth immediately after the return of the browse which has been spread out and exposed to the atmosphere. Fourthly:—The quantity of lime used, should be no more than is just necessary to thicken the browse sufficiently, as it does not in the least contribute to reduce the ore by any chemical reaction; its use is merely to render the browse less pasty, if, from the heat being too great, or from the nature of the ore, it has a disposition to become very soft. Fifthly:—

Coal should be also supplied judiciously, too much unnecessarily increasing the bulk of the browse and causing the hearth to get quite full.

When the ore is of a description to smelt readily, and the hearth is well managed in every particular, it works with but a small quantity of browse, which feels dry when stirred, and is easily kept open and permeable to the blast. The reduction proceeds rapidly with a moderate degree of heat, and the slags produced are inconsiderable; but, if in this state, the stirring of the browse and exposure upon the workstone are discontinued, or practised at longer intervals, the hearth quickly gets too hot, and immediately begins to agglutinate together, rendering evident the necessity of these operations to the successful management of the process. It is not difficult to understand why these effects take place, when it is considered, that in smelting by means of the ore-hearth, it is the oxygen of the blast and of the atmosphere which principally accomplishes the reduction; and the point to be chiefly attended to, consists in exposing the ore to its action, at the proper temperature, and under the most favourable circumstances. The importance of having the ore free from impurities is also evident, for the stony or earthy matter it contains impedes the smelting process, and increases the quantity of slag. A very slight difference of composition of perfectly dressed ore may be readily understood to affect its reducibility; and hence it is that ore from different veins, or the same vein in different strata, as before observed, is frequently found to work very differently when smelted singly in the hearth. It happens, therefore, that with the best workmen, some varieties of ore require more coal and lime, and a greater degree of heat, than others; and it is for this reason, that the forestone is made movable, so as either to answer for ore which works with a large or a small quantity of browse.

It has been stated that the duration of a smelting shift is from 12 to 15 hours, at the end of which time, with every precaution, the hearth is apt to become too hot, and it is necessary to stop for some time, in order that it may cool. At mills where the smelting shift is 12 hours, the hearths usually go on 12 hours, and are suspended 5; four and a half or five bings[*] of ore (36 to 40 cwt.) are smelted during a shift, and the two men who manage the hearth, work each four shifts per week, terminating their week's work at 3 o'clock on Wednesday afternoon. They are succeeded by two other workmen, who also work four 12-hour shifts, the last of which they finish at 4 o'clock on Saturday. In these 8 shifts, from 36 to 40 bings of ore are smelted, which, when of good quality, produce from 9 to 10 fodders of lead. At other mills, where the shift is 14 or 15 hours, the furnace is kindled at 4 o'clock in the morning, and worked until 6 or 7 in the evening each day, six days in the week; during this shift, 5 or 5½ bings of ore are smelted, and two men at one hearth, in the early part of each week, work three such shifts, producing about 4 fodders of lead; two other men work each 3 shifts in the latter part of the week, making the total quantity smelted per week in one hearth from 30 to 33 bings.

Hearth-ends and Smelter's fume.—In the operation of smelting, as already described, it happens that particles of unreduced and semi-reduced ore are continually expelled from the hearth, partly by the force of the blast, but principally by the decrepitation of the ore on the application of heat. This ore is mixed with a portion of the fuel and lime made use of in smelting, all of which are deposited upon the top of the smelting hearth, and are called hearth-ends. It is customary to remove the hearth-ends from time to time and deposit them in a convenient place, until the end of the year, or some shorter period, when they are washed to get rid of the earthy matter they may contain, and the metallic portion is roasted at a strong heat, until it begins to soften and cohere into lumps, and afterwards smelted in the ore-hearth, exactly in the same way as ore undergoing that operation for the first time, as already described.

It is difficult to state what quantity of hearth-ends are produced by the smelting of a given quantity of ore, but in one instance, the hearth-ends produced in smelting 9751 bings, on being roasted and reduced in the ore-hearth, yielded of common lead 315 cwt., and the grey slags separated in this process gave, by treatment in the slag-hearth, 74 cwt. of slag lead, making the total quantity of lead 362 cwt., which is at the rate of 3 cwt. 2 qrs. 23 lbs. from the smelting of 100 bings of ore.

The cost of smelting well-dressed galena at the ore-hearth is as follows:

			s.	d.
Labour			6	1·9
Coals 2·2 cwt.			0	4·4
Wood 1·2 „			0	9·1
Lime 0·6 „			0	3·5
Repairs			0	1·7
Engine Power:	Wages	0 10·7	=1	9·1
	Coals 5·2 cwt	0 10·4		
			9	5·7

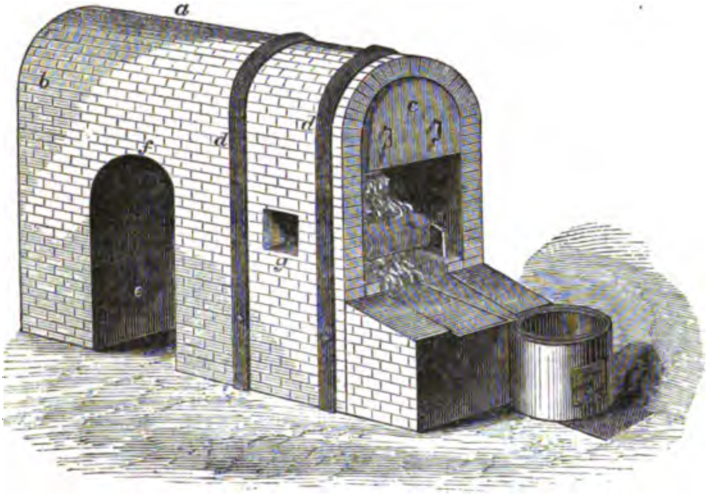
---

[*] 1 bing = 8 cwt.

The ore-hearth, as usually constructed, often allows the fumes to fill the mill, whenever the draught is defective, and thus proves injurious to the health of the work people. Under all circumstances, a large volume of air passes into the flue, and so far diminishes the condensation of the lead-fume.

In order to diminish the objection, the writer introduced the following modifications, shown in *fig.* 610.

Fig. 610.



The hearth is covered with a hood of brick-work, *a*, at the back of which there is an opening into the flue. This opening can be enlarged or diminished by means of a damper, worked from the outside at *b*. The opening in front can also be regulated by means of a movable iron plate, *c*, which can be raised or lowered according to circumstances. The hood is firmly bound by iron straps, *d d*, which are maintained in position by screw-bolts above and below the hearth. The opening *e*, under the arch *f*, allows the workman to regulate the blast, which is admitted at the back through the ordinary tuyere.

The ore is charged through the opening *g*, in the side of the hood, and the furnace is worked from the front, in the manner just described.

We have now finished our account of the reduction of lead ores, and regret that we are compelled to omit many details relating to the various modifications adopted in Germany and elsewhere, which are treated at great length in Kerl's valuable *Handbuch der Metallurgischen Huttenkunde*, to which we beg to refer the reader for further information.

Chemical Reactions in the Blast Furnace.

The substances which compose the charge in blast furnaces, are generally either in the form of powder more or less fine, or in masses more or less fused.

The fume is in the form of powder, and consists chiefly of carbonate and sulphate of lead. The dross and lead skimmings are in coarse powder, and contain oxide of lead, and some metallic lead mixed with the ashes of the fuel and other earthy matters. The furnace-waste contains quartz, clay, and silicate of lead; while the test-bottoms consist either of silicates of lead, &c., or of phosphate of calcium and oxide of lead. The ores and the grey slags are very varied in their composition, containing sulphide and oxide of lead, sulphates and silicates of lead, calcium, barium, &c., and differ as much in their mechanical condition.

The chemical reactions resulting from the fusion of so varied a mixture of compounds, are necessarily of a very complex character, and change even in the different parts of the furnace; thus in the

Upper Zone.—The uncombined oxide of lead, which happens to be present in the furnace in the form of powder, or as a porous mass, is reduced, and as this lead trickles down to the hearth, a considerable portion is volatilised. It is necessary, therefore, in roasting ores, &c., to raise the temperature high enough to fuse them into masses, which are only acted upon, on the surface, by the reducing gases in the upper part of the furnace.

The sulphide of lead is not easily decomposed by the aqueous vapour, and reaches the lower zone almost unaffected. The sulphate of lead stands in the same relation.

The compounds of iron, on the contrary, undergo a striking change, and in fact, play the part of reactives in the lower zone, in consequence of their reduction in this part of the furnace. A high furnace is necessary to complete this reduction, but such a furnace would be unsuitable for lead for the reasons previously given. The size of the pieces of these iron compounds, must therefore be regulated by the height of the furnace, being smaller as the furnace is lower.

Lower Zone.—The matters thus prepared in the upper zone, soften, and gradually enter into fusion as they descend, undergoing very complicated chemical changes which are difficult to regulate, and in which the reducing gases exercise little action, but where the solid fuel comes into operation.

The favourable working of the furnace is also assisted, inasmuch as the materials are not all equally fusible, and do not all soften at the same time. The matters containing the oxide of lead and the slags, melting first, gradually absorb the gangues and produce silicates rich in lead. The sulphates are rapidly decomposed by the melted silicates, and they produce very little sulphides under the reducing action of the solid fuel. Any sulphide of lead present, mixes with the metallic silicates, the reduction of the lead-compounds commencing only after the formation of the silicates. The reducing action is due chiefly to the metallic iron and solid fuel, the sulphides of barium and calcium also assisting in the production of the metallic lead.

Action of the Iron.—This metal decomposes part of the oxide and sulphide of lead, forming sulphide of iron and oxide of iron, which combines with the silicates. The sulphide of iron acts energetically on the silicate of lead, producing sulphurous acid, protoxide of iron, and metallic lead. When the roasting has been complete, there is little or no matt formed, and when a sufficient supply of iron has been produced in the upper zone, the lead is all precipitated and the slags then contain no oxide of lead.

The solid fuel assists the action of the iron, but its contact is of course much less intimate than that of the metal, which ought therefore to be always present in the proportion of an equivalent for every equivalent of lead. Under such circumstances, the slag is very fusible, and does not contain particles of lead, which being reduced in the lower zone the loss by volatilisation is as small as the volatile nature of this metal permits.

The important point consists in the reduction of sufficient iron in the upper zone, without necessitating the employment of a very high furnace. In a *lit de fusion* containing 40 per cent. of lead, there ought to be 9 per cent. of iron in the metallic state or an equivalent quantity of iron ore.

Iron borings, cast iron, &c. have been used, but the proportion of this metal must still be in equivalent quantities to the lead, and they do not act so well as iron finely divided, produced by the reduction of the iron ores.

Action of the Coke.—The reducing action of the solid fuel may be made to take the place of the iron, but unless the gangues and other substances contain sufficient oxide of iron to produce a fusible slag, the latter will consist only of earthy bases, requiring a high temperature for fusion, and thus increasing the loss of lead by volatilisation.

Coke has no action on the sulphide of lead, and as the fuel is charged in large pieces, its reducing action is limited to surface contact. The fuel should therefore be reduced to powder, and intimately mixed with the *lit de fusion*, while the roasting of the lead-compounds should be as complete as possible. This latter operation would, however, require a long time, and its expense would prove a great objection. We made some experiments on this subject, and found that it required upwards of thirty hours' roasting to bring the sulphur, in pure galena, down to 4½ per cent.

The employment of the fuel in powder, is also attended with the inconvenience of a great heat at the furnace-mouth, and the reduction takes place high above the tuyere, which causes a great loss of lead and silver by volatilisation. It is necessary therefore to employ very low furnaces, and to conduct the fusion very slowly; but without the aid of the iron there is always an increased loss of lead, when the reduction depends upon the fuel, and with such furnaces, the iron-compounds act simply as fluxes. On the contrary, in a furnace of suitable height, the intimate mixture of the iron ores and the fuel, is very effective, the whole of the metal acting as a reducing agent.

The reducing action of the fuel is attended with another difficulty, as it facilitates the conversion of the sulphates into sulphides, which then go to form more or less matt. In the case of the sulphates of baryta and lime, the reducing action of the fuel is however, to some extent, beneficial, as these substances assist in decomposing the oxide of lead.

When the matts are poor in lead and silver and not in large quantity, their presence is not very objectionable. We have often worked a furnace where the matt contained only 1·1 per cent. of lead, and 10 dwt. 10 grs. silver per ton. They indicate, when rich, either imperfect roasting in the lead-compounds, or a deficiency of the reducing agents, sulphides of iron, barium, or calcium.

Iron Pyrites as Reducing Agent.—This mineral should be previously roasted to expel a portion of the sulphur, when it is to be used in the blast-furnace, but its employment has a tendency to increase the formation of matt. The same effect is produced, to a greater extent, when the galena employed is loaded with pyrites, since these two sulphides enter into combination in the upper zone of the furnace, and the matt produced does not act so vigorously upon the silicates as the sulphide of iron alone. The matt therefore partly escapes decomposition, and the quantity is accordingly increased.

Fume.—This substance, being in the form of powder, ought not to be charged direct, but it should undergo a preliminary treatment in a reverberatory furnace. It is advisable to mix it with some lead-compounds and a quantity of sand, varying from 15 to 20 per cent., according to its contents in lead. The charge is rapidly heated to the point of fusion, and about 8 per cent. of fuel, in small pieces, added. The whole is then well worked, to mix the fuel as intimately as possible, which promotes the separation of the lead obtained by the reduction of the silicate of lead.

ACTION OF THE GANGUES. *Carbonate of iron.*—This substance is converted, more or less, into sesquioxide of iron during the roasting process, and only interferes with the oxidation of the galena when present in large quantities. It acts in the furnace in the manner already explained, and must be regarded as a useful impurity; but when present in larger quantities and intimately mixed with the lead ores, it prevents the agglomeration of the powder, even when sand is added. Under such circumstances, the reducing action must be moderated in the upper zone of the furnace, and the union of the oxides of iron and lead with some fusible siliceous slags, must be promoted. The furnace ought to be low, and driven with a gentle blast; but with all precautions, there is a tendency to *gob* the furnace.

Iron pyrites.—When this mineral is present, the roasting requires a longer time, and it is difficult to prevent the agglomeration of the ores, with an undue formation of sulphates. Towards the end, the heat must be raised, and the presence of an excess of sand is necessary. The loss of lead and silver by volatilisation in such ores is less, however, probably, from the rapid formation of sulphuric acid by the oxidation of the pyrites, and the conversion of the lead and silver into sulphates.

When the roasting is complete, the only reducing agent necessary in the blast-furnace is coke, the action of which has been previously explained.

The arsenical pyrites is always injurious; the formation of arsenious acid during the roasting, increases the volatilisation of the silver, but the greater part of the arsenic remains behind in the form of arsenates. In the blast-furnace, some more arsenic is volatilised in the upper zone, and part remains combined with the lead and in the matt in the form of arsenuret of iron.

Sulphide of antimony.—During the roasting, the volatility of the antimony increases the loss of lead and silver, and towards the end of this operation, it is impossible to decompose the antimonates, even with an excess of gangues and fusible silicates.

In the blast-furnace, the antimonates are gradually reduced by the gases, the iron, and the solid fuel, with the same facility as the compounds of lead. A part of the antimony is volatilised, by which the loss of lead and silver is increased, and another portion passes into the lead and matt. The presence of this substance necessitates the use of an increased proportion of iron and coke. The antimony also accompanies the lead in all the subsequent operations, although the greater portion can be removed in the calcining process.

Copper pyrites.—In the blast-furnace, the copper is nearly all reduced at the same time as the lead, and when a matt is formed, a portion of the copper is always present. The lead, however, always carries away some copper, which reappears in all the subsequent operations, after giving a characteristic appearance both to lead and litharge.

Blende.—During the roasting, the blende is more rapidly oxidised than the galena, being converted into oxide and sulphate of zinc, which is decomposed with difficulty in the second period, while the infusibility of the oxide impedes the melting of the other materials. It is, therefore, necessary to add some argillaceous compounds to such galenas, and prolong the roasting process. These compounds of zinc are not volatile, but, being infusible, are more liable to be carried off with the current of fume, of which they always form a large proportion; these fumes are richer in silver than those formed in treating similar galenas free from blende. It is not known in what state of chemical combination the silver exists in fume, but from the facts observed in treating ores with different gangues, it would appear that the presence of silver in the fumes is due more to mechanical than to chemical causes.

In the upper zone of the blast-furnace, the oxide of zinc is partially reduced, and as the metal descends, it is volatilised, when it acquires a dark red heat, and burns at the mouth of the furnace, spreading its oxide on all sides. This metal has therefore no beneficial action on the reduction of the lead.

In the lower zone, the oxide of zinc combines with the silica and retards the fusion, while the iron does not easily reduce it, and the metal, once formed, is volatilised without any appreciable action on the silicates with which it comes in contact.

The slags contain some oxide of zinc, which render them of a refractory character. The lead produced, does not contain much zinc, as the temperature is too high to favour the combination of the two metals.

When the roasting has been imperfect, the sulphide of zinc is partially oxidised by the aqueous vapour in the upper zone of the furnace, but the greater portion unites with the sulphide of lead, and forms matt. The greater porosity of these roasted materials, from the presence of the infusible zinc-compounds, increases the reducing action of the gases in the upper zone, and this again adds to the quantity of matt which is formed. This zinc-matt is, however, not so fusible as the others, and consequently remains longer in contact with the silicate of lead, on which it exerts a reducing action, the only benefit derived from the presence of blende.

The volatility of the zinc increases the loss of lead and silver in various ways, by its direct action, as well as by its rendering the roasted materials more porous, in consequence of the infusibility of its compounds in all the operations of roasting, smelting, and treatment of the fume.

The great object therefore in treating such ores is to diminish the chances of volatilisation, by perfect roasting, and the addition of fusible slags in sufficient quantity to overcome the infusibility of the zinc compounds. The beneficial action of iron pyrites in such ores, is due to the facility with which it melts, thus counteracting the opposite tendency of the blende; but the quantity necessary to accomplish this effect may, if the percentage of blende is great, prove so large as to render the ore too poor for any kind of metallurgical treatment.

II. The Refining of the Lead.

All lead ores contain more or less silver, and as the latter metal is reduced along with the lead, its separation becomes an object of commercial importance. The cost of separating silver by the old plan of cupellation, renders it impossible to refine lead with less than eight ounces of silver per ton, and the world is indebted to the late Mr. Pattinson for the discovery of a beautiful process, by which lead with no more than ½ oz. will now pay for its extraction.

The separation of silver, therefore, now involves three operations, viz. desilverisation, cupellation, and the reduction of the pot-dross and litharge.

1. Desilverisation.—Pattinson's *Process.*

This process, known among the workmen as the *separating* process, and called in France, *Pattinsonage*, consists in slowly cooling the melted lead in iron pots, during which a portion of the contents assume a crystalline form, and sink to the bottom. These crystals contain less silver than the portion which remains in a liquid state.

The composition of this desilverised lead, from different localities, is given in the table below.

Analyses of Desilverised Lead.

Locality .	Altenau.	Stolberg.	Billach.	Eschweiler.	Pirsch and Jung.	English.
Analyst .	Streng.	Streng.	Streng.	Streng.	Streng.	Streng.
Lead . . .	99·957	99·935	99·975	99·907	99·892	99·980
Antimony . .	0·021	0·007	0·012	0·053	0·061	0·015
Copper . .	0·016	0·050	0·007	0·026	0·041	trace
Iron . . .	0·006	0·006	0·006	0·003	0·004	0·008
Zinc . . .	trace	0·001	trace	0·011	0·002	0·004
	100·000	99·999	100·000	100·000	100·000	100·010

The pots are large metal pans, and are generally set in a row of 10 or more, those to the left being called the *working* pots, and that to the right, which is smaller, the *market* pot, from the circumstance, that the *poor* lead is ladled from it into the pig moulds, ready for market.

The mode of setting a range of these pots is so clearly shown in *fig.* 611, as to supersede the necessity of any description.

Fig. 611.

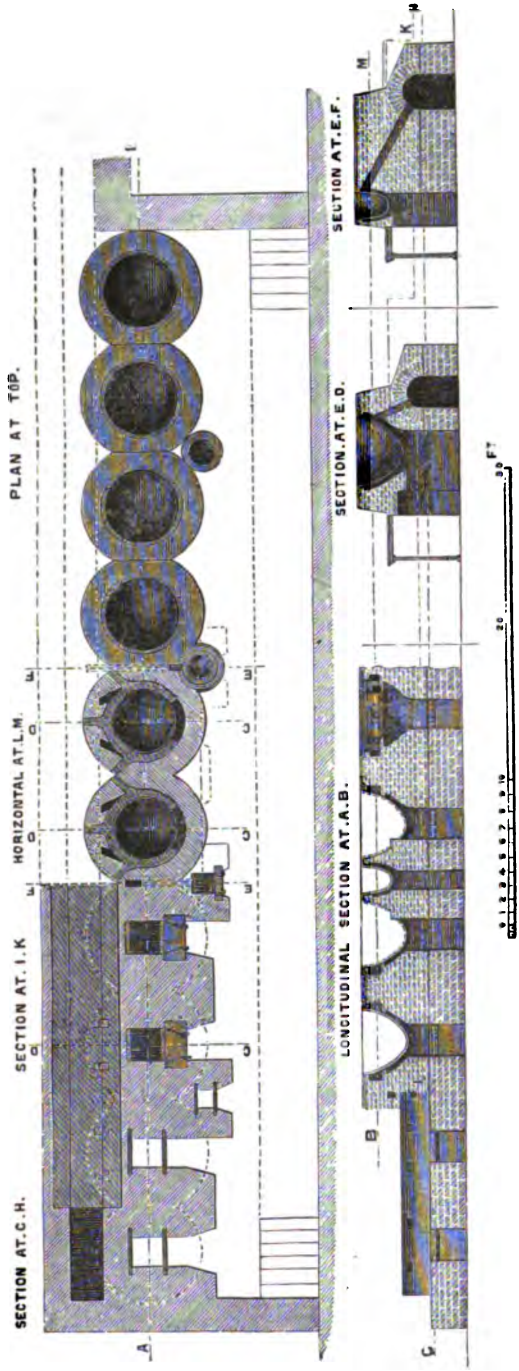
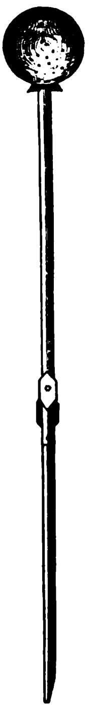


Fig. 612.



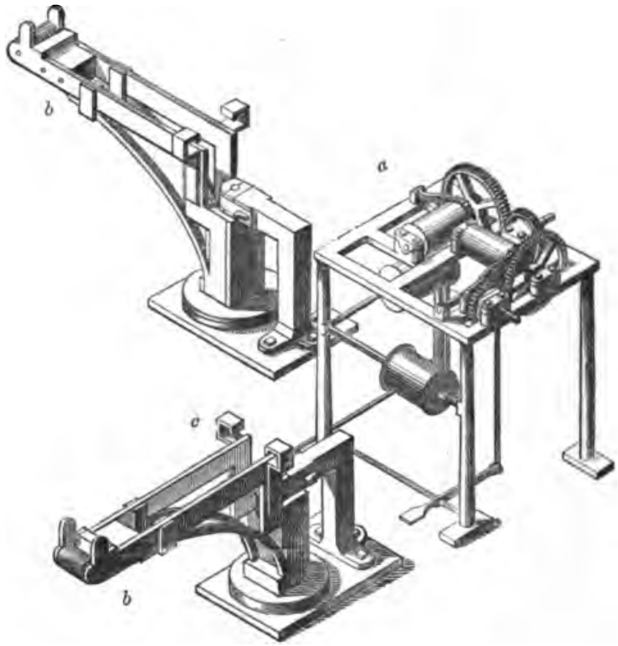
The operation is conducted in the following manner:—One of the pots about the middle of the range is filled with pigs of lead, which are melted. The dross which forms on the surface is skimmed off by a small perforated ladle, when the fire is withdrawn from the grates below this pot. The lead, as it cools, is constantly stirred, and any portion which solidifies round the edges, is removed by an iron paddle or *slice*, and mixed with the molten lead. In a short time, the crystals, above mentioned, make their appearance, and continue to increase in quantity as the cooling progresses. The workman then dips a large perforated ladle, represented in *fig*. 612, into the mass of liquid lead and crystals, and withdrawing it, allows the liquid portion to drain away, which he hastens by an occasional shake of the ladle. He then attaches to the shank of the ladle, a hook, which is suspended at the end of a chain hanging upon the joists of the roof, and holding on by the handle, swings the ladle full of crystals over the next pot to his right, into which he empties the crystals. He continues this operation until the necessary quantity of lead has been crystallised out, when the liquid portion is ladled into the adjoining pot on his left. The same operation is repeated with all the intermediate pots, until the desilverised lead arrives at the market-pot, and the enriched lead reaches the rich pot, whence the lead is taken for cupellation.

The proportion of lead crystallised out in each pot varies very much with the richness of the lead at the command of the refiner, and especially if he has *original* leads of different values, by which he can keep up a continuous supply of lead to each pot. When the original lead is poor, then what is known as the *low system*, is adopted, where as much as seven-eighths of the lead is separated; but with richer lead, the *high system* is followed, and as little as two-thirds is removed as crystallised lead.

During the operation, the large ladle is liable to cool by its repeated exposure to the air, and in consequence the perforations become closed by the adhesion of the lead. This difficulty is overcome by occasionally dipping the ladle into the small intermediate pots on the one side, which are kept full of lead, maintained at a higher temperature by a small fire beneath them, as shown in *fig*. 611.

The shaking or jerking of the large ladle by the workmen when draining the crystals, would ultimately injure the pot, to protect which, a pig of lead with a bar of iron cast in its upper surface, is laid on the broad rim of the pot, and this serves at the same time as a fulcrum on which the shank of the ladle rests.

Fig. 613.



These pots often require to be renewed, and as a large weight of metal in the rims is rendered useless in each renewal, the upper portion of the brickwork is covered in some works with a circular metal slab, on which the narrow rim of the pot rests, by which a saving of expense in the repairs is effected.

This process is also accompanied by another advantage in purifying the lead. Each time the lead is melted, the surface becomes covered with a scum, which contains more or less impurity along with the oxide of lead, and this dross being always skimmed off, the quality of the lead is continuously improved as it approaches the market-pot. This circumstance is so well recognised, that leads containing only one ounce silver per ton, and even less, are regularly treated by this process, especially when the lead is to be used in the manufacture of white lead.

An average cost, founded on the crystallisation of 1,917 tons of lead containing 24 ounces of silver per ton, was found to be as follows:

	s.	*d.*
Labour	9	7·6
Coals, 6·2 cwt.	1	0·4
Repairs	0	2·9
	10	10·9

Stagg's apparatus.—The expense of labour is an important item in Pattinson's process, and none but powerful men are capable of managing the crystallising ladle. This objection attracted the attention of the late Mr. I. D. Stagg, who succeeded in constructing an apparatus for obviating this difficulty. This arrangement, known as *Stagg's apparatus*, is represented in *fig.* 613; it consists of a crane and windlass, *a b*; a chain attached to the end of the shank of the ladle is wound up by the windlass, and draws up the ladle, filled with crystals, out of the pot. A workman guides the handle of the ladle, which is afterwards placed under a catch, *c*, of the crane. While the crystals are draining, the ladle is occasionally shaken by the workmen, and by moving the crane, the ladle is easily carried over the adjoining pot, into which the crystals are emptied.

Worsley's apparatus.—This gentleman has also patented arrangements by which the labour is economised. He fixes an upright shaft in the centre of the pans, with a bearing at top and bottom, while arms radiate from the shaft to the sides of the pans; with this apparatus he obviates the use of the slice.

The other plan consists in drilling a ¼ to ½ inch hole horizontally through the side of the pan, about two inches above the bottom. The opening inside the pan is covered with a sheet-iron strainer screwed down to the pan, and a spout is set in an opening made through the side wall of the fire-hole of the pan, to carry off the liquid lead into a pot placed outside. The hole in the pan is made tight by a slightly tapering *tapping bar*. The crystals remain behind for further treatment.

Parkes' *Process.*

This process depends upon the superior attraction of silver for zinc over lead, and is applied by Mr. Parkes in the following manner:

The silver-lead is melted in one of the large pans already described, and raised to the temperature of melted zinc. The zinc being melted, is then added, and the fluid metals are stirred for a period of one to two hours. The fire is now lowered and the metals allowed to cool down until the lead is about to set. The zinc and silver rise to the surface during the interval, and are removed by means of a perforated ladle.

This alloy is afterwards heated in a sloping iron retort to remove a portion of the lead, which contains 1,000 ounces of silver per ton, and is ready for cupellation. The portion left in the retort, is heated in clay pots to distil off the zinc. The residue contains silver mixed with the impurities of the original lead and zinc. It is melted with lead and cupelled to obtain the silver.

Mr. Parkes also proposed to roast the alloy in close retorts or muffles, by which it was reduced to a fine powder, which was then to be treated with dilute sulphuric acid. The foreign oxides dissolved in the acid, leaving the silver, which was treated in the usual way.

The quantity of zinc required to desilverise the lead, depended upon the proportion of silver and other metals present in the lead, and he gave the following statement in his specification—viz. for 20 cwt. of lead containing

14 oz. of silver per ton	22·4 lbs. of zinc.
21 „ „ „	33·6 „
28 „ „ „	44·8 „

The loss of lead in this process is said to be about 1 per cent., but on account of the difficulty in treating the alloy of zinc and silver, Messrs. Neville are understood to have abandoned the plan.

Separation of Copper in Crystallisation.

Mr. Baker has published the following results of an inquiry to ascertain how far the impurities of lead, viz. silver, copper and iron, are removed in this process of crystallisation.

The original lead contained:

	1	2
Silver	0·0046	0·0052
Copper	0·0066	0·0154
Iron	0·0065	0·0068
Sulphur	trace	trace.

The various products of the process contained:

	Silver.	Copper.	Iron.
Rich Pot:—			
Before crystallising	0·0108	0·0344	0·0312
Crystals, 25 pts.	0·0052	0·0152	0·0086
Fluid lead, 85 pts.	0·0140	0·0476	0·0122
Second Pot:—			
Before crystallising	0·0052	0·0154	0·0068
Crystals, 95 pts.	0·0020	0·0066	0·0118
Fluid lead, 25 pts.	0·0126	0·0286	0·0146
Third Pot:—			
Before crystallising	0·0020	0·0102	0·0118
Crystals, 70 pts.	0·0010	0·0038	0·0198
Fluid lead, 25 pts.	0·0100	0·0240	0·0082
Fourth Pot:—			
Refined lead	0·0014	0·0054	0·0112

From this Mr. Baker very naturally draws the conclusion that there is an alloy of copper-lead which remains fluid when crystals of lead are formed, and that when the former metal is present in moderate proportions, it may be separated from the latter by a process similar to that of Pattinson.

This statement has been disputed by Reich and Streng, who deduce from their experiments the conclusion, that the copper is not separated; but the writer, without having analysed the different leads, inclines to believe in the correctness of Mr. Baker's conclusions.

2. Cupellation or Refining of the Rich Lead.

Although it may be difficult to assign a correct interpretation to Hebrew terms of art, yet we think it is clear that the use of lead in purifying other metals was known in very ancient times. Jeremiah would seem to allude to this fact in the passage in ch. vi. ver. 29, and similar reference is made in Ezekiel xxii. 18–22, Malachi iii. 2, 3. The first notice of the process of cupellation among the ancients, appears in the works of Dioscorides; and Pliny and Geber describe an operation which is a true cupellation by means of lead. In 1343, Philippe le Bel issued an ordinance prescribing the use of cupels for testing the precious metals. In 1556, Agricola in his work, *De re Metallica*, fully describes the whole process, with instructions how to make the tests; this was followed by the work of Barba, *Arte de los Metales*, in 1640, where the construction of the refining furnaces is minutely explained.

The chief object is generally to separate the silver from the lead, but when an oxide of lead in the form of litharge is wanted, then the former becomes a secondary operation.

There are many modifications as to the form of furnace, mode of refining, &c., but only what may be called two distinct methods of cupellation—viz. the English and German.

The English System.

The peculiarities of this system consist in the cupel being movable, and the lead being fed at intervals.

The furnace, which is termed a *Refinery*, is represented in *figs.* 614, 615, where two cupels can be worked at the same time when necessary; *a a* are the positions of the cupels or tests, one of which is shown resting on an iron waggon, *b*; *c c*, the pots containing the rich lead in a melted state, which is ladled into an iron gutter, *d d*, to supply the test; *e e*, the point where the blast enters, and *f f* the opening or *gate*, through which the litharge is blown over into a pot below; *g g*, the fire grates, and *h h* the ash pits; *i i*, the flues, and *k k* the chimneys.

Fig. 614.

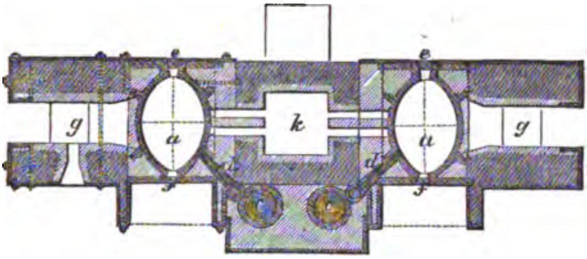
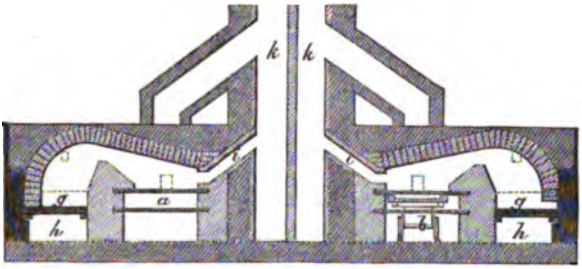
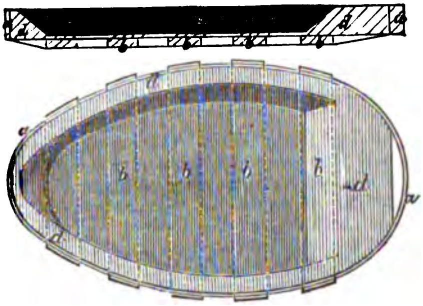


Fig. 615.



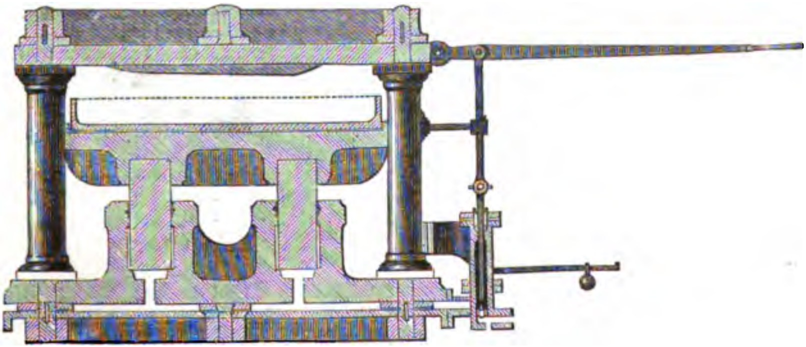
The bottom or sole of this reverberatory furnace is formed of bone-ash, finely ground, which is prepared by moistening it with a very weak solution of pearl-ashes. This mixture is placed within an oval iron frame-work, formed of an iron ring *a a*, (*fig.* 616) about four inches deep, called the *test-ring*, and iron bars cross the bottom *b b*. The bone-ash mixture is then carefully and firmly beaten down with iron rammers. The centre of this mass is then scooped out by means of a small trowel, as seen at *c*, and the portion round the sides and ends, *d d d*, left as walls to retain the melted metals.

Fig. 616.



As the success of the cupellation depends in a great measure on the careful preparation of the cupel, an apparatus has been contrived to give a proper consistence to the bone-ash. A longitudinal section of this apparatus is shown in *fig.* 617 in such detail as to render any description unnecessary. It is worked by hydraulic pressure.

Fig. 617.



The test is allowed to dry in the air for some time, and then placed on the waggon, which is run into position. The test is then wedged tight up against an iron ring built firmly in the masonry. The fire is now lighted and the test carefully annealed, otherwise it is liable to crack. When perfectly dry, it is heated to a dull redness, and then filled with the melted rich lead.

This lead soon becomes coated with a greyish dross, but as the heat increases, the surface of the lead appears, and the formation of litharge commences. The blast is now turned on, and while supplying the oxygen necessary for the oxidation of the lead, it drives the litharge to the mouth of the refinery, where it flows in a continuous stream over the gate into a little iron pot placed on wheels for the convenience of removal.

When there is only enough rich lead to yield a small cake of silver, the refining is completed in the same test, and in that case, the workman cuts down the opening in the bone-ash at this end of the test, which is called the gate, to the level of the melted lead, until the *fining* of the silver commences.

When there is a stock of rich lead, the concentration of the silver is confined to the first test, which is called the *lead-test*. As soon as the silver amounts to about 8 per cent. of the contents of the test, a small hole is carefully drilled in the bottom, and the rich alloy is run into moulds. The hole is then closed by a pellet of bone-ash, and another cupellation commenced. The rich alloy is afterwards refined in the same manner in another test, hence called the *silver-test*.

When the lead has been nearly all oxidised, the film of silver becomes thinner and thinner; it then exhibits a succession of the beautiful iridescent tints of Newton's rings, and at length the film of oxide disappears, revealing the brilliant surface of silver beneath. Such is Dr. Miller's admirable description of this beautiful phenomenon, known as the *fulguration* of the metal, or as the men call it, the *brightening of the plate*.

At this point the blast is turned off, the fire withdrawn, and the silver allowed to cool. When the silver has *set* and begun to harden, the wedges are removed, and the test with its cake of silver falls on the iron waggon. When cold, it is removed, the impurities adhering to its under surface are chipped off, and the silver is ready for fusing into ingots.

During the cupellation, the silver absorbs oxygen, which is evolved as the metal cools, forming crater-like eruptions on the surface, and the extent of these protuberances is a very good indication of the purity of the silver.

There is not much silver lost in the refinery by volatilisation, but a comparatively large absorption takes place in the test. We have assayed several test-bottoms, and have found the contents in silver to vary from 74 oz. to 115 oz. per ton of test.

Chambers' Steam Blast.—The blast employed in refining must be soft, and is best supplied by means of a fan, but a very excellent plan of Mr. Chambers was tried by the writer, and furnished very good results. It consisted in substituting a steam jet for the blast of air, and as the steam passed through a wide nozzle, it carried sufficient air along with it to oxidise the lead, while mixing a body of steam with the lead fume, which was thus more completely recovered in the long flues by the condensation of the steam.

A more simple and compact form of refinery is shown in *figs.* 618, 619, where the steam blast-pipe is represented entering the furnace at *a*. This refinery is also fitted with an iron hood, *b*, placed in front of the working door, where occasional puffs of fume are blown over the workman. This fume is carried off by an iron pipe, *c*, into the chimney, and this protects the men from the injurious consequences of inhaling the lead smoke.

The following statement as to the cost of refining, is founded on the cupellation of rich lead, which produced upwards of 60,000 oz. of fine silver:

		s.	*d.*
Labour		3	10·3
Coals	4·7 cwt.	0	9·4
Pearl-ashes	0·6 lbs.	0	4·0
Bone-ashes	18·7 „	3	3·8
Repairs		0	2·0
Engine Power:	Coals cwt. 5·2 = 0 10·4 Wages . . 1 0·3	= 1	10·7
Per ton of lead		10	4·2

or 3*s.* 1·1*d.* per 100 oz. of silver.

When the silver has been removed, the test is broken up, those portions of the bone-ash which are free from lead, being removed for subsequent use, and the rest is generally carried to the slag-hearth or blast-furnace, where the bone-ash of course is lost. Mr. Johnson recovers this bone-ash as follows:—

Johnson's Process.—He reduces the cupel to a powder, and mixes it with acetic acid of 1·030 to 1·048 specific gravity, in sufficient quantity to render the mixture of a thin consistence to admit of its being well agitated in a dolly tub. The greater part of the lead dissolves, and by renewing the acid, a further quantity is removed, so that, on working the residue to separate all the solution, the bone-ash is sufficiently pure to be employed again in making tests. The solutions yield the lead, in the form of sugar of lead, by concentration.

Fig. 618.

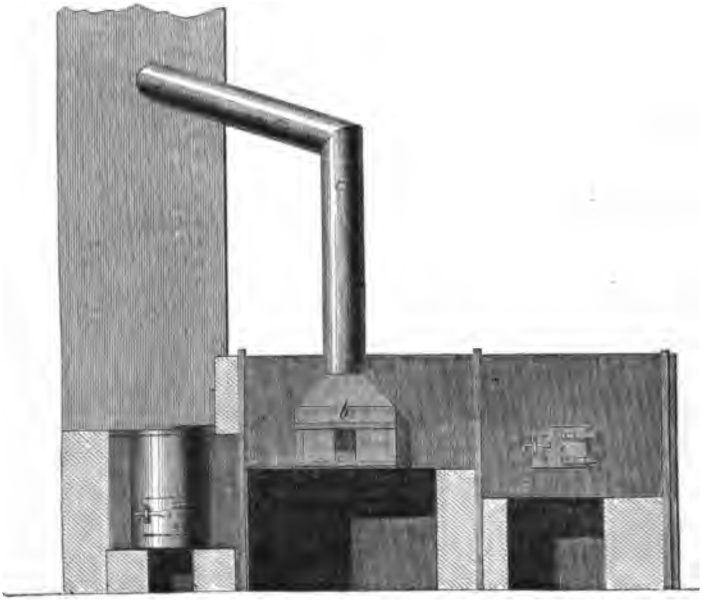
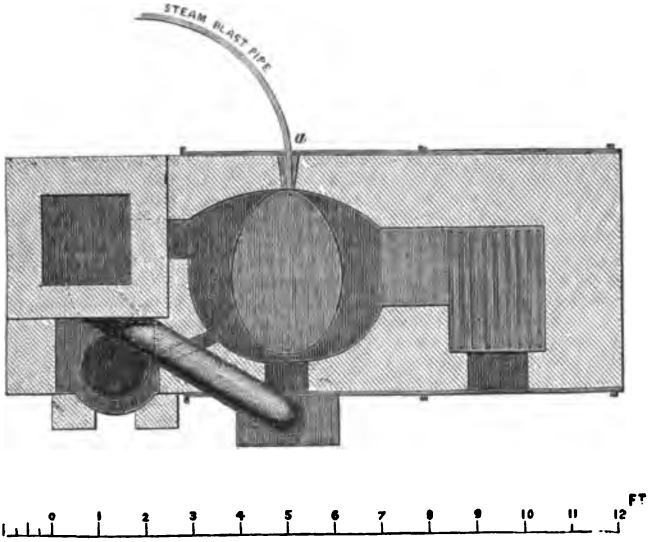


Fig. 619.

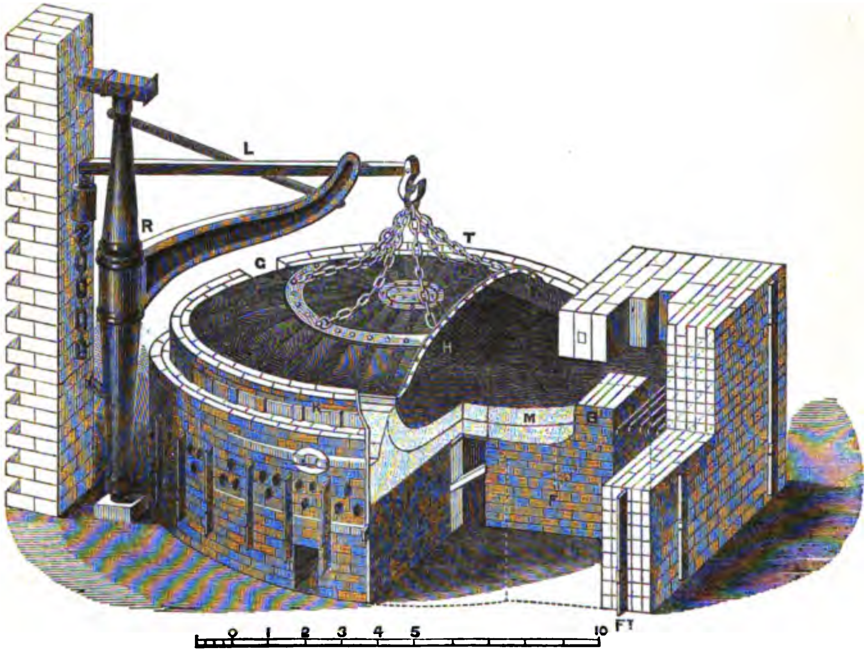


The German System

differs from the English in forming the hearth of marl instead of bone-ash; and in making it of large dimensions, and charging all the lead at one time.

The form and construction of this furnace is shown in *fig.* 620, which is taken from an excellent treatise on the Metallurgy of Lead by Dr. Lamborn. The corner on the right is removed, to show the interior. The circular portion contains the hearth and a rectangular fireplace. The foundations, F F, are built of stone, cramped with iron rods, and pierced with openings to carry off the moisture. A, represents the fireplace, in which either wood or coal can be burnt. The hearth is formed of bricks set on edge on a bed of scoriæ which has been well beaten down. A layer of marl, also carefully beaten with iron rammers, is formed on the bricks, and this bed is generally renewed at each cupellation. A wall, K K, surrounds the hearth, and serves to support a movable cap, C, which is formed of sheet iron, strengthened by bars on its upper side, and lined with clay secured by numerous iron straps. The cap is suspended by chains from the crane, R, and supported by a lever, L, so that it can be raised or removed on one side, when necessary. The opening, G, opposite the fire-bridge, B, serves to introduce the materials of which the hearth is constructed, as well as the lead to be refined, and acts as a chimney to carry off the products of combustion. The workman watches the operation through an opening in the corner, which is removed in the woodcut, through which the vapours pass away. The blast enters at T, through two tuyeres, whose nozzles are frequently covered by two small valves, called *butterflies*, to diffuse the blast over all the surface of the bath.

Fig. 620.



When all is ready for work, a thin bed of straw is laid upon the hearth, on which the pigs of rich lead are piled. The cap, C, is then lowered on the walls, and fluted with clay all round the edges. The fire is then lighted, and soon after the lead is melted, its surface is covered with a dark crust called *abzugs*, consisting of the oxides of the foreign metals, and other impurities from the lead. This crust is drawn off through the working door, opposite T. The fire is kept up to maintain the lead at a dark-red heat, while the impurities, termed *abstrichs*, continue to separate. The table which follows, contains the analysis of some of these products. The next product which appears, is known under the name of *cupreous* or *wild Litharge*, and at the end of some hours, the formation of the true litharge commences. The heat is now maintained between a cherry and a bright red, until the operation is complete.

Analyses of the Products of Cupellation.

Technical names .	*Abstrichs.*								*Abzugs.*	
Locality . . .	Poullaouen, 1st.	Poullaouen, last.	Holzapfel, 2nd.	Villefort.	Freiberg.	Katzenthal, 1st.	Katzenthal, last.	Pontgibaud.	Poullaouen.	Pontgibaud.
Protoxide of lead . .	63·60	84·40	68·00	82·00	95·50	67·60	88·80	89·50	36·10	53·1
Oxide of copper . .	. .	0·80	trace	. .	0·50	0·40	. .	0·20	4·60	1·1
Oxide of zinc . . .	7·00	5·20	. .	. .	1·10	0·20	. .	1·50	5·00	4·6
Sesquioxide of iron . .	. .	. .	4·00	. .	0·30	4·40	. .	2·60	5·10	5·4
Alumina	. .	.	with Sil. acid	. .	. .	with Sil. acid	with Sil. acid	. .	0·80	
Lime	. .	.	14·00	. .	. .	7·60	5·00	. .	0·70	
Antimonic acid . .	28·60	9·00	14·00	17·60						
Teroxide of antimony .	. .	. .	. .	. .	. .	. .	. .	. .	4·80	0·5
Arsenic acid . .	. .	. .	. .	. .	2·30	19·70	6·20	0·70	. .	3·0
Silicic acid . . .	1·60	. .	. .	. .	. .	. .	. .	. .	5·80	
Sulphur	. .	. .	. .	0·40	. .	0·30	. .	. .	6·80	C, 5·6
Metallic lead . . .	. .	. .	. .	. .	. .	. .	. .	. .	32·40	23·0

There are two varieties of litharge obtained, distinguished by their colour, *yellow* and *red*, the former being in fused pieces, while the latter is in flakes. The difference arises from their mechanical condition, which results from a difference in the cooling.

Analyses of Litharge.

Locality .	Freiberg, yellow.	Halsbrücke.			Clausthal.	Unter-Harz, last.
			red.	black.		
Authority .	Kersten.	Plattner.	Rammelsberg.		Brüel.	Ulrich.
Protoxide of lead .	96·21	. .	96·35	94·68	99·69	58·13
„ of copper .	0·82	0·95	1·35	0·59	0·40	0·28
Sesquioxide of iron .	0·41	. .	0·66	0·59	trace	35·25
Oxide of bismuth .	. .					
Protoxide of zinc .	1·31					
Protoxide of silver .	0·003	. .	. .	. .	. .	0·71
Arsenious acid . .	1·21	1·56				
Teroxide of antimony	. .					
Silicic acid . .	. .	. .	0·45	0·59	. .	3·75
Carbonic acid . .	. .	. .	2·70	2·00		
Lime. . . .	. .	. .	0·49			

The period when the operation approaches a termination is marked by the brightening of the melted mass, when some hot water is thrown over its surface, and as soon as the silver begins to solidify, cold water is used to harden the cake. This silver contains 2 or 3 per cent. of lead, and is refined by another process.

Separation of Lead from Bismuth.

This process of cupellation has been employed by Patera to separate the two metals, lead and bismuth. At Joachimsthal in Bohemia, the small quantity of bismuth in the ore gradually accumulates in the rich lead, and when the latter is submitted to cupellation, a green litharge makes its appearance towards the end of the operation. This substance, called "Black Litharge," is reduced and refined in the usual way. The lead is first oxidised, and leaves the bismuth, nearly pure, on the test. This impure metal is refined in a second cupellation, and the bismuth so obtained is very pure, as indicated by the following analysis:

Bismuth .	99·58
Silver .	0·42
Lead . .	trace
Iron . .	trace
	100·00

The original alloy obtained by reducing the black litharge, consists of:

Bismuth .	34·5
Lead . .	65·5
	100·0

The progress of the cupellation is carefully watched, and samples of both the litharge and the metal on the test are analysed from time to time. The mixed metals are dissolved in nitric acid, and an excess of hydrochloric acid is added to convert the metals into chlorides. Strong alcohol is added, which precipitates the chlorides of silver and lead, and the bismuth is thrown down from the solution by carbonate of ammonia, then filtered, and weighed.

Manufacture of Litharge.

An oxide of lead is in demand for the preparation of acetate of lead and other purposes, and this substance is produced in two forms, as *Flake* and *Levigated* litharge.

Flake Litharge.—When litharge is manufactured for sale, the purest lead, not rich in silver, is selected for cupellation. The refining process is conducted as already described, but the oxide of lead at the commencement and termination of the cupellation is rejected.

The litharge, as it flows from the test, is received in large pots fitted on wheels, in which it is allowed slowly to cool. In some cases, the pots are heated so that the cooling may be more gradual, as the proportion of the flake litharge depends upon this condition. When the pots are emptied, the mass of litharge falls, and the whole is passed through a circular temse, working in a close wooden erection to protect the men from the dust. The fine flake litharge is collected and packed in casks.

Levigated Litharge.—The portion of litharge which does not fall, but remains in hard fused pieces, is employed for the manufacture of levigated litharge.

The process consists in simply grinding this fused litharge between horizontal stones with a supply of water. The mill employed for the purpose is seen in *figs.* 621, 622.

Fig. 621.

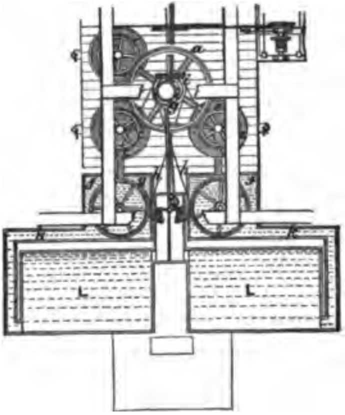
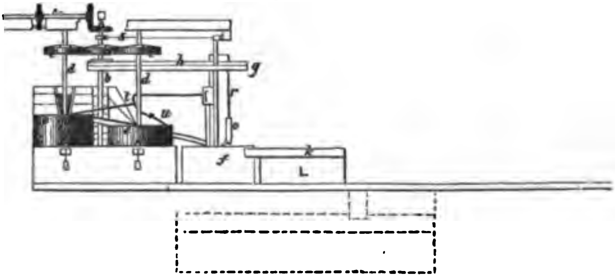


Fig. 622.



Motion is communicated to the driving wheel, *a*, on the upright shaft, *b*, which works into the wheels, *c c c*, on the spindle *d d d*, turning the upper stones of the three pairs *e e e*. The litharge, along with a small stream of water, is fed into the lower pairs, as it is seldom necessary to pass it through two sets of stones. The ground mass then falls into the dolly-tubs, *f f*, which are agitated by means of the sheaves, *g g* driven by the belts, *h h*, working round a sheave, *i*, on the upright shaft. The levigated litharge flows away with the water along the spouts, *k k k k*, and deposits in the large tanks, L L, which are kept full of water. The overflow escapes at *m*, into the cisterns, *n n*, in which there are three pumps, *o o* and *p*, all worked by gearing, *r*, *s*, in connection with the main shaft. The water from the pumps, *o o*, supplies the dolly-tubs, for washing the litharge and promoting the separation of that portion which is coarse, which separation is completed in the broad spouts, *k k k*. The pump, *p*, supplies water for mixing with the litharge as it enters the eye of the stones, through the pipe, *t*, and for washing the outside cases and rims of the stones, through the pipe *u*.

When the tanks are filled with litharge, they are allowed to stand for some time. The litharge subsides and the water is run off by plugs or siphons. The litharge is then removed and dried at a very low heat in a reverberatory furnace. It is afterwards packed in casks lined with paper.

3. Reduction of the Pot-dross and Litharge.

In the previous operations, more or less of the lead is converted into an oxide, in the form of dross in the desilverising pans, and as litharge in the cupellation.

The furnace in which these substances are reduced resembles the smelting furnace, and is of the ordinary reverberatory character. The sole slopes from the fire-bridge to a point near the flue, where an iron gutter is inserted in the brickwork, which is never closed, and through which the lead runs into an iron pot on the outside, whence it is ladled into pig moulds.

This furnace is shown in section and plan in *figs*. 623, 624, where A represents the fireplace; B, ash-pit; C, fire-bridge; D, hearth; E, working door; F, the iron spout; G, the pot outside heated by a small fire below.

Fig. 623.

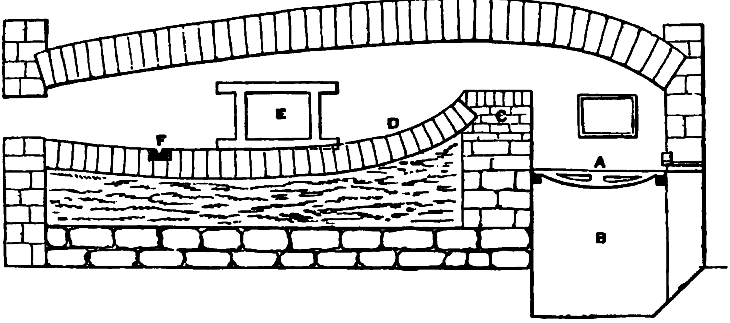
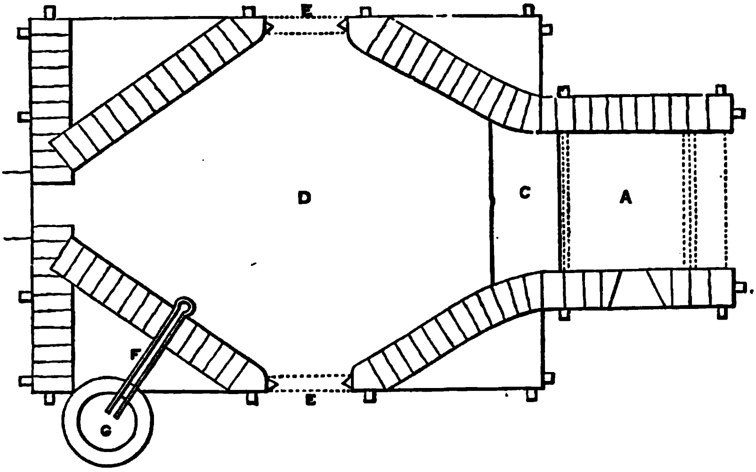


Fig. 624.



The sole is covered with a small quantity of coal, on which a mixture of the oxides and coal is thrown near to the fire-bridge. The ignition of the fuel and the reducing gases in the furnace soon causes a reduction of the metallic oxides, and the liquid metal trickling down through the porous mass, finds its way to the point, F, whence it flows into the metal pot, G. The charge is frequently turned over by an iron rake to present fresh surface to the reducing action of the fuel, and to facilitate the escape of the lead. Fresh charges are introduced during the shift, and at the close of the day, the residual matters, termed *cinders*, are raked out.

In smelting works, there ought to be at least three of these reducing furnaces, in which the oxidised products of the different operations can be reduced, viz., one for pot-drosses, another for litharges, and a third for calciner's dross, to be described in the next section. This necessity arises from the difference in the quality of the lead produced, and which, by being mixed, would afterwards entail an unnecessary expense.

The dross is reduced in precisely the same way as the litharge, but when it is very impure, the addition of a little soda-ash facilitates the operation and increases the produce of metal. The dross from the poor pans must also be kept distinct from that of the rich pans, as the difference in the contents of silver saves some expense in the subsequent desilverisation of the two leads.

The same remark applies to the litharge, especially that which flows off towards the conclusion of the cupellation.

The cost of reducing litharge and pot-dross is nearly the same, and the following details may be taken as an average:

	s.	*d.*
Labour . . .	2	8·7
Coals, 4·1 cwt. . .	0	8·2
Repairs . . .	0	1·0
	3	5·9 per ton.

III. Softening of hard Lead.

All the lead produced at the blast-furnaces, and some leads obtained from poor ores in the reverberatory furnaces, are so hard from the presence of impurities or other causes, as to render them unfit for treatment in the desilverising process. The lead obtained from the English slag-hearth (p. 520) is also of the same character, and, until within about the last twenty years, was sold for running lead-joints, &c., irrespective of its contents in silver. The composition of some of these hard leads is given in the following table:

Analyses of Hard Leads.

Authority.	Bie-wend.	Müller.		Rich-ard-son.	Ker-sten.	Bi-schoff					Streng.	Rich-ard-son.	Streng and Overbeck.	
Locality .	Alten-auer.	Unter-harz.	Ober-hütte.	Eng-lish.	Frei-berg.	Holz-apfel.	Katz-enthal.	Ville-fort.	Pesey.	Pont-gibaud.	Claus-thal.	Span-ish.	Lau-terthal.	Andre-asberg.
Lead . .	83·91	84·72	82·40	99·27	91·51	81·27	91·40	95·60	93·00	91·4	85·34	95·81	83·65	77·75
Antimony .	16·01	10·32	10·04	0 57	5·32	16·40	8·20	2·40	7·00	8·2	14·06	3·66	16·00	21 27
Arsenic .	. .	2·00	3·00	. .	1·02	. .	0·40	. .	. .	0·4				
Copper .	0·04	1·68	2·28	0·12	0·90	2·29	. .	traces	traces	. .	. .	0·32	0·13	0·16
Iron . }	0·04	0·82	1·08	0·04	0·62	0·04	. .	. .	. .	. .	0·10	0·21	} 0·30	0·42
Zinc . }												. .		
Sulphur .	. .	. .	. .	. .	0·20									

The writer having carefully examined the W B slag-lead, found that its hardness was mainly due to the presence of antimony. He then suggested the erection of furnaces in which this lead, in a melted state, could be exposed to a current of hot air. The result was the production of a good soft lead, at so reasonable a cost as to render the process available as a regular operation in smelt mills.

Soon afterwards, the first cargoes of the now well-known Spanish hard lead arrived at Liverpool; but the smelters there would not purchase them, and one cargo was tran-shipped to Newcastle-on-Tyne. This lead could not be softened in the brick furnaces, being so fluid when melted, as to find its way out of the furnace in all directions. The late Mr. G. Burnett, who consulted the writer on the subject, and witnessed the treatment of the slag-lead at Mr. Beaumont's works at Blaydon, then proposed the simple but admirable plan of lining the furnace with a metal pan. Thus was laid the foundation of a trade with Spain, which has gone on increasing, until, it is said, upwards of 20,000 tons of this description of lead are annually produced in that country.

Calcination of the Lead.

The furnace generally employed in this operation, termed *calcining* or *improving* by the workpeople, is represented in the *figs.* 625, 626 in elevation and vertical section. A is the fireplace; B, ash-pit; C, fire-bridge; D, cast-iron pan; E, flue; F F F, channels for the escape of moisture; G, a working door; and H, the spout for running off the soft lead.

The lead is either thrown into the pan in pigs, or previously melted and ladled into a spout, which carries it to the pan. The charge varies from 6 to 10 tons, and the time required for calcination depends upon the quality of the lead. With English slag lead, a few hours are sufficient, and the writer has witnessed a charge of hard lead, obtained from reducing the dross of previous operations, require 30 days for softening.

Fig. 625.

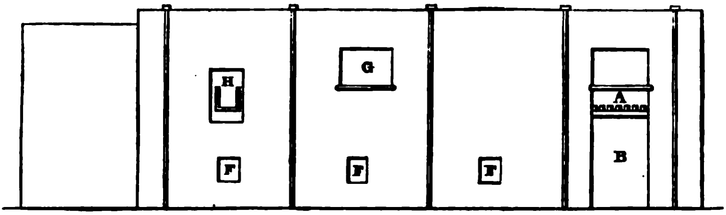
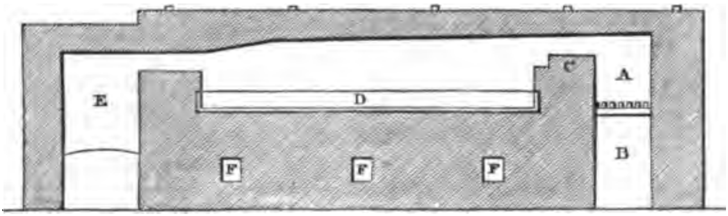


Fig. 626.



As soon as the furnace is at a working heat, the surface of the lead becomes coated with the impure dross, which is removed by skimming, and withdrawn through the working door. If the lead is very impure, this dross floats in a semi-fluid state on the surface of the lead, and must be dried up with a little lime to bring it into a condition capable of being removed. The workman dips a ladle into the lead when he thinks the calcination is about complete, and pours it into a mould. The sample is

Fig. 627.

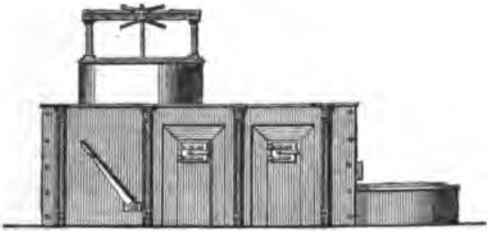
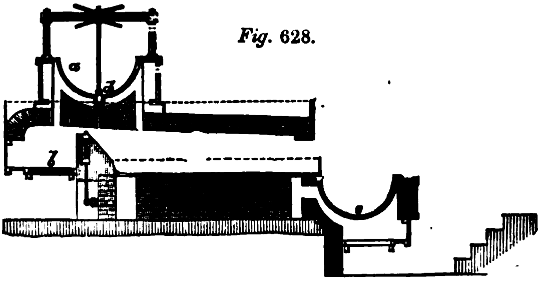


Fig. 628.



examined when cold, and if it is soft to the scratch, with a flaky, crystalline appearance on the surface, the contents of the pan are ready to be run off through the iron spout, into a pot on wheels, whence it is ladled into pig moulds.

An improvement has been made on the above simple form of furnace, which is shown in *figs.* 627, 628, representing a front view and a longitudinal section. The hard lead is melted in the pot, *a*, which is heated by the fire, *b*. The calcining pan, *c*, is supplied with melted lead from the pot by raising the plug, *d*. The soft lead is run into the pot, *e*, and then cast into pigs. This form of furnace possesses great advantages when softening extra-hard lead, as the calcining pan can easily be kept always full, with very little labour.

The produce of soft lead from the hard leads, of course, varies greatly, as will be seen from the following table, which contains the results of the treatment of many hundreds of tons of most of the descriptions named:

Good Spanish hard lead	93·2	per cent.	soft lead.
Hard lead from crystallising dross . .	90·3	„	„
Hard lead from economic furnaces . .	84·3	„	„
English slag lead	87·1	„	„
Slag lead from Spanish dross . . .	66·9	„	„
Slag lead from refuse products . . .	67·3	„	„
Tea lead	76·4	„	„

We have mentioned tea lead as among the hard leads which can be treated by this process, and we have found that tin is as easily separated thereby as antimony.

The following hard leads were mixed and submitted to calcination:

	tons.	cwt.
Ordinary Spanish hard lead	1436	9
Ore slag lead	100	18
Dross „	69	12
Spanish „	60	9
Mill „	128	16
English „	75	15
Tea hard lead	9	15
Fume „	3	19
tons	1885	13

At a cost, per ton, for:

	s.	*d.*
Labour	2	5·3
Coals, cwt. 5 . . .	0	10·0
Repairs	0	1·6
	3	4·9

Pontifex and Glassford's Process.—These gentlemen employ the ordinary calcining pan-furnace, and when the charge has been in operation for a few hours, the dross being removed as usual, a few pounds of the following mixture is spread evenly over the surface of the bright lead. The doors are closed, and in about 10 to 20 minutes, a brown or yellowish-brown cake collects on the surface. Fresh fuel is then thrown on the fire, and in a few minutes, when the smoke has cleared away, the doors are opened, and the cake is removed. This is repeated until the cake formed possesses a bright or brown colour. When the alkaline mixture is used, with a charge of 9 or 10 tons of lead, about 55 lbs. are required during the 24 hours' operation. When the other mixture is employed under the same circumstances, the quantity required varies between 40 and 60 lbs.

The mixtures recommended are as follows:

1. For lead containing from 3 to 15 per cent. of antimony, the mixture consists of:

3	parts of	nitrate of soda.
4	„	soda-ash.
4	„	burnt lime.

2. For lead containing 2 to 3 per cent. of antimony, and from ½ to 1½ per cent. of silica, the mixture consists of equal parts of soda-ash and caustic lime.

We understand that this process has been discontinued, and if it be true that the antimony exists in the hard lead in the form of an alloy of antimony and lead, which when the whole is melted, rises to the surface in consequence of its lower specific gravity, we cannot see how the time of softening should be shortened with advantage, at the extra cost of so expensive an oxidising agent as nitrate of soda. In the old mode of working, when the surface of the lead is kept constantly clear of dross by the calciner, the alloy, as it rises, is immediately oxidised by the current of hot air, whereas in this process, a considerable time is lost in allowing the mixture to act, and before the crusts are removed.

Mr. Barker of Sheffield has, however, succeeded in using the nitrate of soda and bisulphate of soda to advantage in this process, possibly from the fact that the impurities in his lead are so much smaller than in those of Spain, and by performing the operation, it is said, in crucibles.

Reduction of the Dross.

This process is performed in an ordinary reducing furnace, of smaller dimensions than usual, as the charges are smaller and require more attention to prevent the loss of antimony by volatilisation. The writer also introduced the use of a little soda-ash with the coal, when mixed with the dross, which was found to render the slag which is formed, more fusible, and enabled the workman to work at a lower heat. The following analyses of the hard lead obtained from this dross, with and without the addition of this flux, prove the advantage of its employment:

	Without the soda-ash.	With 2½ per cent. of soda-ash.
Lead	82·88	58·70
Antimony	16·09	40·66
Copper	0·68	0·32
Iron	0·35	0·32
	100·00	100·00

With the use of this flux, and continuing the calcining operation on the produce of the reducing furnace, the metals obtained were found to possess the following composition, according to the analyses of the writer:

English Hard Lead.

	Original lead.	1st calcination.	2nd calcination.
Lead	99·27	86·53	52·84
Antimony	0·57	11·29	47·16
Copper	0·12	traces	traces
Iron	0·04	0·34	traces
	100·00	98·16	100·00

Spanish Hard Lead.

	Original lead.	1st calcination.	2nd calcination.
Lead	95·81	64·98	56·60
Antimony	3·66	29·84	43·40
Copper	0·32	5·90	traces
Iron	0·21	0·20	traces
	100·00	100·92	100·00

It was found impossible to separate any soft lead from the product of the second calcination, all the metal becoming oxidised. This alloy is found of great use in casting type furniture, and in making some of the coarser kinds of type.

The cost of reducing the dross, per ton of lead produced, is as follows:

	s.	d.
Labour	5	2·1
Coals, 7·6 cwt.	1	3·2
Soda-ash, 34 lbs.	2	1·5
Repairs	—	
	8	6·8

Separation of the Antimony.

Instead of reducing the dross which yields the lead of the second calcination, the writer proposed to grind it to powder, and treat it with acetic acid, by which all the lead is dissolved, and yields sugar of lead by evaporation and crystallisation. The insoluble residuum, when reduced in the usual method employed for antimony ores, furnishes this metal very readily, and of fair quality.

The same process is applicable to the separation of the oxide of tin when the dross has been formed by treating tea lead.

Cost of treating Spanish Hard Lead.

The Spanish hard-lead trade has assumed such an important development, that in concluding this account of the treatment of hard lead, it may not be without some interest to give the cost of extracting its silver, and preparing the soft lead for market.

The cost of each item of expense is calculated on 20 cwt. of the original hard lead: thus the second item is on 5 per cent less; the third, on 9 per cent.; the fourth, on 35½ per cent; the fifth, on 7 per cent. of the original lead; the seventh, eighth, and ninth items are an average on the whole work of the establishment. A similar statement has been published elsewhere, but in the absence of the above information, it must have been unintelligible to most readers.

Cost of Softening and Refining Spanish Lead.

	£	s.	d.
1. Calcining	0	3	4·9
2. Crystallising	0	10	4·4
3. Refining	0	0	11·1
4. Reducing litharge and pot-dross .	0	1	2·8
5. Reducing calcining dross . . .	0	0	7·2
6. Smelting refuse products . . .	0	0	4·2
7. Grinding materials	0	0	5·8
8. General labour	0	2	4·1
9. General charges	0	3	8·2
	£1	3	4·7

IV. Smelting of the Slags and other Products.

All the waste products resulting from all the previous operations—viz. ore or grey slags from the reverberatory furnace and ore-hearths, test-bottoms, litharge and dross cinders from the reducing furnaces, &c., are finally submitted to a process of reduction, in this country in a furnace known as the slag hearth, but abroad they are generally mixed with poor lead-ores, and smelted in a blast furnace. We will describe the method adopted in this country, and then select one of the continental plans as an illustration of the other method.

1. *The English Slag Hearth*

is known among the Germans as the *Krummofen*, or crooked furnace, and among the French as the *fourneau-à-manche*, or elbow-furnace. The general form and construction of this furnace are shown in *figs*. 629, 630, &c. It somewhat resembles the ore-hearth.

Fig. 629.

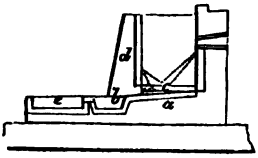
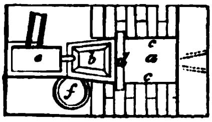


Fig. 630.



Hearth.—The sole-plate, *a*, is made of cast iron, and slopes slightly down to the fore-hearth, *b*. There are strong cast-iron pieces, or *bearers*, *c c*, on each of the long sides of the sole-plate, which support the side walls as well as the cast-iron plate, or *forestone*, *d*, which forms the front of the shaft. The back is made of cast iron up to the horizontal tuyere in the middle, above which it is built of sandstone. A cistern, *e*, stands in front of the fore-hearth, and a stream of water constantly flows through to granulate the slag, and facilitate the subsequent separation of any pieces of lead disseminated through it by washing. The lead flows over the fore-hearth into an iron pot, *f*, heated rom below by a fire.

The bottom of the furnace is filled with small cinders, beaten down, and reaching to within 4 or 5 inches of the tuyere. The pot is also filled with similar cinders, which filter the lead from the fusible slags which sometimes accompany the metal. Peat is then piled up above the bed of cinders, ignited, and the blast turned on.

When the peat is ignited, some coke is thrown in, and a layer of grey slag or other refuse lead product is added. This is continued at intervals as the operation proceeds, alternate layers of slag and fuel being added, metallic lead being produced, and a fusible slag, free or nearly free from lead. The smelter occasionally forces a bent iron bar through the layer of cinder, to liberate the slag, which flows off into the water cistern.

The lead obtained is always very hard and impure, and is afterwards sent to the calcining process for softening.

When cold air is employed in smelting, it is often difficult to prevent the nose of slag at the tuyere from growing too long. The use of hot air prevents this inconvenience, and also economises the expense of this operation, as the following comparative statements will prove:

a. 28 tons of slag smelted with cold air consumed 392 cubic feet of air per minute, and cost:

	£	*s.*	*d.*
Labour	3	7	8
Coke 7 tons at 24*s.* 6*d.*	8	11	6
	11	19	2

b. 35 tons of similar slag with hot air, consumed 300 cubic feet of air per minute, and cost:

	£	*s.*	*d.*
Labour	3	7	8
Coke, 5 tons. 17 cwt. at 24*s.* 6*d.*	7	3	4
Turf for heating air, 11 loads at 1*s.* 8*d.*	0	18	4
	11	9	4

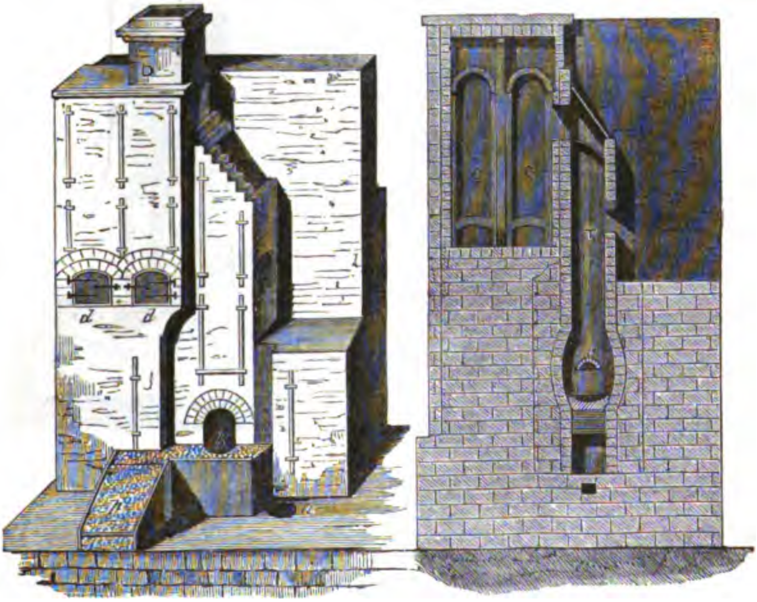
The saving is therefore very considerable when hot air at 500° to 600° F. is employed.

2. *The Clausthal Blast Furnace.*

This furnace varies in height from 20 to 25 feet, with a diameter of 3 feet in the widest part. The crucible at the bottom of the hearth projects beyond the blast of the furnace into a small elevated platform in front. The lining of the hearth is made of fire-stone, and the bottom is slightly hollowed. This part is covered to some depth with a mixture of fire-clay and charcoal, with a gentle slope from the back to beyond the front wall of the furnace. A tap-hole enters at the lowest part of this basin, through which the contents are drawn off.

The receiving basin, *a*, is placed on a level with the floor, and at some distance from the breast of the furnace, which is supplied with air forced through the tuyeres at *t*.

Fig. 631.



The charge of mineral is thrown towards the side of the tuyere, and the fuel towards the breast. The cold air from the tuyeres cools the slags, and forms channels round their nozzles, six or seven inches long, which are called the "nose of the tuyere." The success of the operation greatly depends upon the proper management of this point, as these channels prevent the oxidation of the lead, which would give rise to the formation of fusible silicates of lead.

Under all circumstances, a large quantity of lead is volatilised, and the whole of the vapours escaping from the tunnel-hole, T, pass through a series of chambers, C C, before entering the chimney, D. The fume which condenses is occasionally removed through the doors, *d*, and is again thrown into the furnace along with other products.

The scoriæ flow continuously into the fore-hearth, where they solidify and are drawn down the inclined plane, *p*, by the workman, to the floor of the mill. When the basin, *b*, becomes filled with metal, it is tapped into the reservoir, *a*.

The products which are collected in the outer basin consist of lead, upon which a matt floats. This matt solidifies first, and is removed for further treatment, when the lead is passed through a metal sieve, and cast into pigs.

The matt contains sulphides of lead and other metals, and when they accumulate, they are roasted in heaps to expel the sulphur; but so imperfect is the operation, that some portions must undergo as many as four roastings.

When the roasting is finished, the residue is smelted in the German slag-hearth, along with test-bottoms and other waste products. The *lit de fusion* is composed of:

32	parts of	roasted matt.
80	„	rich grey slags.
4·5	„	test-bottoms.
2	„	abstrichs.
2	„	litharge-cinders.
1	„	granulated cast iron.

The furnace used in the smelting of these products is shown in *figs.* 632—634. It is

Fig. 632.

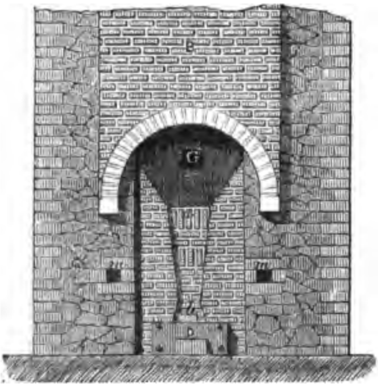


Fig. 634.

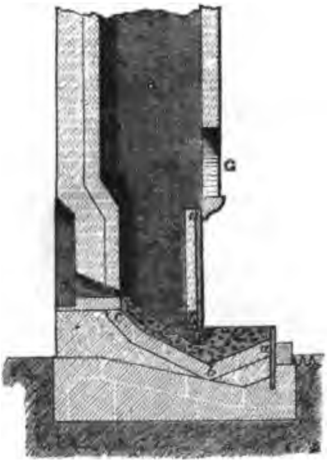
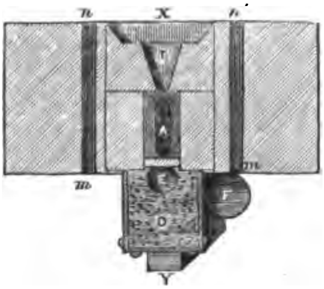


Fig. 633.



about 4½ feet high, and increases in size in the upper portion, C. *Fig.* 633, represents a horizontal section at the level of the tuyere, and *fig.* 634, a vertical section in the line XY. It is blown with one tuyere, T. From the bottom of the furnace, which is *brasqué*, the contents are drawn off by a tapping hole into the pot, F.

The fuel employed is coke, and during the smelting, part of the iron of the matt combines with the silica of the slags and cinders, forming a new, very fusible slag. Another portion of the iron reduces the sulphide of lead, producing metallic lead and a second matt.

The following table contains the analyses of some slags made in smelting cupel bottoms, &c.:

Analyses of Lead-slags from Blast Furnace.

Authority .	Brüel.	Berthier.		Karsten.	Berthier.			
Locality .	Clausthal.	Poullaouen.		Harz.	Pontgibaud.			
Silica . . .	28·75	35·20	34·80	40·00	38·70	20·00	22·00	38·70
Oxide of lead . .	44·60	26·80	6·60	34·80	7·40	traces	35·60	16·00
Protoxide of iron .	6·87	19·40	34·40	5·60	28·40	37·90	4·20	23·70
Oxide of manganese .	0·42	0·60	0·60	3·00	2·40			
Suboxide of copper .	0·21	. .	. .	1·60				
Alumina . . .	8·92	4·60	4·80	12·90	8·70	10·00	5·20	11 60
Lime . . .	7·83	4·40	7·00	1·00	12·80	4·40	30·20	9·00
Magnesia . . .	0·53	. .	. .	0·90	0·60	. .	1·00	1·00
Teroxide of antimony	0·70							
Oxide of zinc . .	. .	5·20	0·50					
Protosulphide of iron	. .	2·20	9·00					
Sulphide of zinc .	. .	. .	. .	. .	. .	10·20		
Baryta . . .	. .	. .	. .	. .	. .	17·50		

This matt is treated in the same manner as before, but in the fourth matt the copper has accumulated to such extent, that it is called the *copper matt*, and is treated for that metal.

This accumulation of copper is always observed, however small the percentage of copper in the original ore. The copper, having a stronger affinity for sulphur than lead, goes on accumulating in these matts, and generally pays for its extraction.

The mixture smelted in these Clausthal furnaces, consists of:

34 parts of ore containing 24 of galena.
4 to 5 „ cupel bottoms.
1 „ the abstrichs from the refinery.
39 „ ore slags.
4½ „ granulated cast iron.

which mixture is stated, by Regnault, to produce 19 pts. of metal, and 7 or 8 pts. of the first matt, containing 2¼ pts. of metal.

V. Condensation of the Lead Fume.

Since attention has been drawn to the great loss of lead in smelting its ores, numerous plans have been proposed to recover a portion of the metal in the form of fume, no fewer than sixteen patents having been enrolled for this object.

Where sufficient space exists, the plan most generally adopted is that of long flues and chambers. In some cases these flues extend for 5 miles. In Mr. Beaumont's extensive works, his able engineer, Mr. Sopwith, added nearly 5 miles of flue to one mill, the flue being 8 ft. high by 6 ft. wide. The saving in lead in these flues of Mr. Beaumont, is said to exceed £10,000 per annum.

Of the many plans which have been suggested, we will select two which are in successful operation.

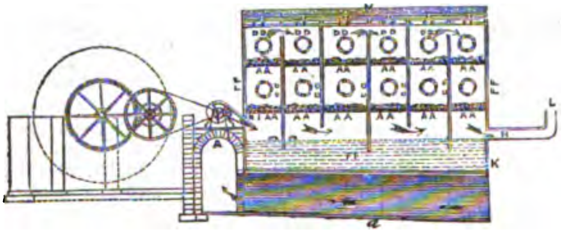
1. *Stokoe's Condenser.*

This apparatus is represented in *fig.* 635, and has been found to answer remarkably well at Langley mill, as the details of an experiment, given on p. 525 amply prove.

A is the top of the fume-flue; B is a wheel fixed in a metal case, set in motion by steam or water power, with a speed of 10,400 revolutions per minute, by which the fume is withdrawn from the flue and forced through the condenser. This condenser is rectangular, divided longitudinally by wooden rails, A, A, laid horizontally, on which a layer of pebble-stones, or other filtering material, is placed. The condenser is further separated into compartments, D, D, by the vertical divisions, C, C, which alternately reach the top, and dip below the surface of the water. The water flows from an open trough, M, divided crossways, immediately above D D, into the compartments, E, E, each of which is again subdivided by four or more low parallel partitions. The bottom of these cisterns, E E, is perforated. The water is supplied by a pipe, D G, and the bottom of the condenser is kept filled with water to the level shown at F F.

The fume is withdrawn from the flue, and forced up and down through the filtering beds, in the direction of the arrows, until the residual gases escape at H, into the chimney, L. These fumes, in their passage through the condenser, come in contact with the water from E E, which is constantly falling in fine showers over the filtering beds. The water carries down all the fume into the reservoir, F F, whence it is occasionally drawn off at K.

Fig. 635.

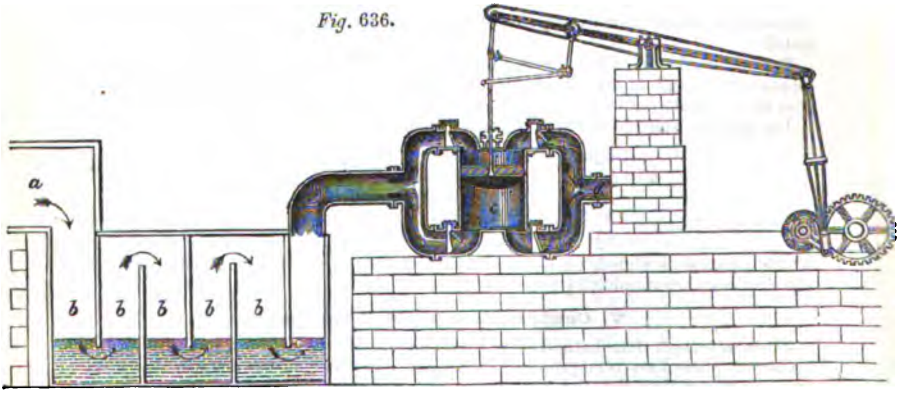


The following table (p. 525) gives the results of an experiment, on the large scale, with one of these condensers.

Stagg's Condenser.

This apparatus is represented in *fig.* 636, in which *a* is the fume flue, *b b b b*, a cistern constructed of wood or any other material, with partitions, dividing it alternately at top and bottom; *c*, one or more air-pumps, or exhausting machines; and *d*, the exit-flue for the uncondensed gases. The air-pumps being set in motion, the fume is drawn through the water in the cistern, in which the metallic vapours are condensed, so perfectly, that the writer has walked along the exit-flue without being soiled with a single particle of fume. The passage of the vapours under the water creates a great agitation and spraying of the water, which materially assists in the condensation. When the water becomes charged with fume, it is drawn off by cocks, and run into tanks to allow the fume to subside.

Fig. 636.



Mr. Stagg has drawn up the following table from his experiments, to show the annual saving of lead which may be effected by his condenser, and the volume of gases for which the exhausting apparatus must be constructed:

Nature of furnace.	Quantity of lead operated upon or produced per annum.	Volume of smoke emitted from such furnace per minute.	Annual saving effected on each operation in lead.
	tons.	cubic feet.	tons.
Ore hearth . . .	250	1,000	12½
Reverberatory . .	500	1,500	20
Refining and reducing.	500	1,500	35
Slag hearth . . .	200	3,000	40

Experiment made at Langley Smelt Mills upon 298 *Bings, or* 267,008 *lbs. of Lead Ore, to show the utility of a Condenser placed* 1,056 *yards from the Smelt Mill.*

Blast Hearth Process.	Weight In lbs. Avoirdup.	Weight Foth. cwt. qr. lb.	Per cent.	Rate of Foth.	£ s. d.	Blast Hearth Process.	Weight In lbs. Avoir.	Weight Foth. cwt. qr. lb.	Per cent.	Rate per Foth.	£ s. d.
Total weight of ore operated upon	267,008			£						£	
Produce of lead by assay .	202,258 or	85 20 3 14	75·75	18	1,547 17 3						
,, ,, by blast hearth	178,895 or	76 1 1 3	67·00	,,	1,369 1 10	Taken from the condenser. Produce of lead from condensed fumes	11,000 or	4 14 1 6	47	18	84 5 0
Total loss of lead and value in smelting . . .	23,363 or	9 19 2 11	8·75	. .	178 15 5						
Refining Process.											
Total weight of lead refined	37,632 or	16 0 0 0	. .	. .	288 0 0	**Refining Process.**					
Produce of lead from litharge	32,592 or	13 18 0 0	. .	. .	249 8 7	Taken from condenser.					
Total loss of lead and value in refining . . .	5,040 or	2 3 0 0	13·40	. .	38 11 5	Produce of lead from condensed fumes	2,375 or	1 0 0 23	47	. .	18 3 6
Reducing Process.											
Total weight of dross reduced	43,008 or	18 6 0 0	. .	. .	329 2 0	**Reducing Process.**					
Produce of lead from the dross	41,468 or	17 13 1 0	. .	. .	317 6 0	Taken from condenser.					
Total loss of lead and value in reducing . . .	1,540 or	0 13 3 0	3·60	. .	11 16 0	Produce of lead from condensed fumes	725 or	0 6 1 25	47	. .	5 10 6
Loss in blast hearth process	. . . . .		. . .	. .	178 15 5	Saved from blast hearth process	. . . . .		. .	. .	84 5 0
,, ,, refining ,,	. . . . .		. . .	. .	38 11 5	,, ,, refining ,,	. . . . .		. .	. .	18 3 6
,, ,, reducing ,,	. . . . .		. . .	. .	11 16 0	,, ,, reducing ,,	. . . . .		. .	. .	5 10 6
						Balance in long flue slags, &c., as proved by actual experiment.	. . . . .		. .	. .	121 3 10
					229 2 10						229 2 10

The composition of the fumes produced from different operations and localities, is given in the following tables:

TABLE I.—*Analyses of Fumes from the Reverberatory Furnaces.*

Locality . . .	Pontgibaud.		Alston Moor.	Conflans.	Redruth.	Freiberg.
Authority . . .	Berthier.	Rivot.	Berthier.			Rammelsberg.
Protoxide of lead . .	11·00	. .	10·20	42·60	71·20	34·93
Sulphate of lead . .	60·00	39·00	65·60	39·00	. .	Arsenic & antimony 0·60
Arsenious acid . .	2·00	1·50				
Sesquioxide of iron . .	12·00	. .	3·40	. .	traces	Protoxide 3·80
Oxide of zinc . . .	15·00	2·70	13·80	. .	. .	27·15
Carbonate of lead . .	. .	35·00	. .	. .	. .	Lime 0·71
Sulphate of zinc . .	. .	2·30	. .	. .	. .	Magnesia 0·39
Sulphide of lead . .	.	4·50	1·40			
Oxide of copper . .	. .	. .	. .	. .	0·20	
Alumina	. .	. .	. .	. .	1·20	
Silicic acid . . .	. .	13·20			20·60	31·82
Clay	. .		5·60	17·40		

TABLE II.—*Analyses of Fume from the Refinery.*

Locality	Pontgibaud.		Villefort.	Freiberg.
Protoxide of lead . . .	88·20	40·00	71·20	48·30
Sulphate of lead . . .	9·00	20·00	17·80	
Arsenious acid	0·30	3·00		14·40
Oxide of antimony . . .	4·40	. .		3·90
Oxide of zinc	. .	. .	. .	25·70
Oxide of bismuth . . .	. .	. .	. .	0·50
Carbonate of lime . . .	3·70	17·00	. .	
Carbonic acid	. .	. .	5·00	4·50
Silicic acid	3·40	20·00		
Clay			4·60	

TABLE III.—*Analyses of the Fumes from the Blast Furnaces.*

Locality	Freiberg.	Pontgibaud.			Halsbrücke.	Pontgibaud.
Oxide of lead	27·90	10·00	66·50	3·70	1·50	80·10
Sulphate of lead	13·00	47·00	. .	13·00	. .	9·00
Arsenious acid	2·10	. .	1·10	1·50	. .	4·10
Sesquioxide of iron	. .	. .	3·00	13·00		
Oxide of zinc	49·50	10·00	12·00	3·10	95·00	
Carbonate of lime	. .	. .	. .	. .	. .	2·80
Carbonic acid	7·00					
Sulphuric acid	. .	. .	17·00			
Silicic acid	. .	33·00	. .	. .	1·50	4·90
Sulphur	. .	. .	. .	8·90		
Metallic lead	. .	. .	. .	55·40		

STATISTICS OF THE LEAD TRADE.

1. *Great Britain.*

The following tables from Mr. Hunt's valuable Annual Report, give all the information we possess as to the home trade in this metal:

Summary of Lead and Silver Produce, 1862.

	Lead ore.		Lead.		Silver.
	tons.	cwts.	tons.	cwts.	ounces.
ENGLAND.					
Cornwall	6,030	5	4,119	0	205,662
Devonshire	2,079	1	1,376	5	39,265
Somersetshire	750	0	375	0	1,025
Shropshire	4,157	11	3,103	8	
Derbyshire	7,048	10	5,028	9	1,000
Yorkshire	9,255	1	6,313	10	3,331
Staffordshire	60	2	37	4	
Westmoreland	2,017	12	1,375	12	17,148
Cumberland	7,173	13	5,241	10	41,911
Durham and Northumberland	21,771	18	16,454	0	82,854
WALES.					
Caermarthenshire	1,298	10	1,009	9	4,046
Cardiganshire	8,299	11	5,443	2	62,678
Pembrokeshire	339	12	255	0	1,790
Brecknockshire	2	0	1	10	
Montgomeryshire	4,288	19	3,269	10	21,020
Merionethshire	197	0	150	14	650
Denbighshire	7,925	0	6,236	2	27,148
Flintshire	5,211	18	3,997	8	31,333
Caernarvonshire	236	8	170	11	988
ISLE OF MAN	2,508	12	1,861	0	70,592
SCOTLAND	1,767	5	1,262	6	6,190
IRELAND	2,643	2	1,763	2	12,481
Sundries under ten tons	250	0	170	0	1,360
Total of the United Kingdom	95,311	2	69,013	12	632,472
			Value.		
Silver ore from British mines	200	7	£15,095	5 5	53,651
Total of silver	. .	. .	. .	. .	686,123

Imports and Exports of Lead, Foreign and Colonial.

Lead imported into the United Kingdom in the year 1862 and two previous years.

Quantities.			Declared value.		
1860	1861	1862	1860	1861	1862
tons.	tons.	tons.	£	£	£
22,171	23,109	23,693	468,435	440,092	460,536

Exports of British Lead for the year 1862, *and two previous years.*

Countries to which sent.	Quantities.			Declared value.		
	1860	1861	1862	1860	1861	1862
	tons.	tons.	tons.	£	£	£
Russia	4,812	3,875	3,033	109,622	80,635	62,847
France	1,116	665	518	24,197	13,889	10,261
United States	4,157	767	12,687	88,531	16,156	259,947
China and Hong Kong	5,171	5,644	9,728	114,035	122,788	208,196
British India	1,317	1,820	2,347	31,799	40,077	51,921
Australia	1,615	1,493	1,593	39,434	33,347	34,760
Other countries	5,609	5,031	6,442	135,681	116,529	142,658
Total	23,797	19,295	36,348	543,299	423,421	770,590

2. *France.*

A large trade is carried on in this metal between Marseilles and the adjoining coast of Spain. The latest statement we can find of this trade in France, is for 1859, when the eight principal mines produced 2,400,000 kilog. of dressed ore. The exports and imports in the same year were as follows:

Imports.

		Ore.		Lead.
Sardinian States	kilog.	17,983,849	kilog.	168,217
Spain	„	2,040,069	„	33,447,682
Algiers	„	3,856,258	„	
Belgium	„	1,961,118	„	655,833
Germany	„	253,123	„	
England	„	201,659	„	887,262
Other countries	„	24,972	„	320,341
Netherlands	„		„	2,033,238
	kilog.	26,321,048	kilog.	37,512,573

Exports.

		Ore.		Lead.
Spain	kilog.	1,537,740	kilog.	
The Two Sicilies	„	231,796	„	1,094,302
Sardinian States	„	258,115	„	1,080,139
United States	„	. .	„	7,597,242
Austria	„	. .	„	1,014,618

3. *Other Countries.*

It is difficult to obtain accurate statements of the production of lead in many countries, and the following statement can only be regarded as approximative:

	tons.
United States	20,000
Prussia	16,000
Austria	7,000
Spain	60,000
Italy	5,000*
Russia	350
Sweden	40

In conclusion, we give a list of patents which have been taken out for improvements in the dressing, smelting, &c., of lead ores:

Patents for Improvements in Preparing Ores, &c.

Date.	Patentee.	Object of Patent.
1777	Thomas . .	Machine for stamping slags.
1779	Roe . . .	Calcining galena (and other sulphides), in kilns, preparatory to dressing.
1830	Petherick . .	An apparatus for washing ores.
1832	Petherick and Kingston	Further improvements on the apparatus patented in last.
1841 1842 and 1844	Brunton . .	Machinery for washing and dressing ores.
1849	Rowlandson .	Removing zinc and copper from lead ores, by roasting and washing with water and acid, before smelting for lead.
1852	Richardson .	Roasting galena dead before smelting, in a five-flat furnace, the ore to be placed at first in the highest or coolest, and gradually brought to the heat as it loses sulphur.
1860	Goble and Hemming	Improved stamps.

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* There were also 10,000 tons of galena exported from Italy in the same year.—T. R.

Patents for Improvements in the Construction of Furnaces.

Date.	Patentee.	Object of Patent.
1638	Wagoner . . .	Saving of fuel by improved furnace.
1827	Somers . . .	Furnace formed of slag, with iron pan for bottom.
1828	Brunton . . .	Calcining furnace with revolving bottom, and a mechanical arrangement for stirring the ore.
1841	Merry	Applying the waste heat from coke ovens to smelting of lead or other ores.
1841	Welsh	Splitting the draught in a reverberatory.
1850	Parkes . . .	Revolving apparatus for stirring the ore while being calcined on a fixed floor, the apparatus being made hollow to allow the passage of a current of air to keep it cool.
1852	Richardson . .	Small blast-furnace for reduction of certain lead-residues, &c.
1855	Jenkin . . .	Improvement in furnaces, enabling the waste heat from a smelting hearth to be employed, when desired, in a calciner.
1858	Jenkin . . .	Further improvements on the above.

Patents for Improvements in the Smelting Process.

Date.	Patentee.	Object of Patent.
1630	Ramseye . . .	"To make separation by taking off the second scum of all such metals as tin, copper, and lead, after the dross is taken, and preserving as well the impure metal as the pure."
1687	Clerk, Brent, and Clerk	Treating poor argentiferous and auriferous lead ores.
1697	Lydall	Improvements in desilverising lead ores, followed by conversion into litharge or red lead.
1774	Sanderson . .	Obtaining from argillaceous matters and lead-slag, &c. the metal, by a process in which a matt of sulphide of iron seems to have been produced.
1803	Clayfield . . .	Separating the lead from arsenical compounds (oxidised), by lime and coal.
1845	Napier . . .	Decomposing the fused ore by electricity (lead not specially mentioned).
1858	Phillips . . .	Extracting lead, &c. from the residue left in distilling some ores of zinc.

Patents for Improvements relating to the Flux, Fuel, &c.

Date.	Patentee.	Object of Patent.
1632	Jorden . . .	Smelting lead and other ores by pit-coal, peat, or turf.
1676	Hutchinson . .	Improvements in smelting lead and other ores with pit-coal.
1678	George, Lord Grandison	Substitution of pit-coal, &c. for wood, in reverberatory furnaces.
1690	Hodges . . .	Same claim as the last.
1847	Parkes . . .	Treatment of galena with chloride of barium or calcium, mixed with carbon and iron.
1849	Young . . .	Addition of oxide of iron to coal in smelting carbonates of lead containing silica, galena, and lead slags, antimonial or otherwise.
1852	Richardson . .	Reducing the oxides from the calcining process with alkali and coal.
1852	Pattinson . .	Reducing the residues from preparing oxychloride of lead by common salt and granulated iron.
1854	Cookson . . .	Treatment of galena with "alkali or neutral salt and carbonaceous matter, and iron," employing the resulting sulphide of iron to obtain sulphurous acid.
1856	Pope	Employment of the residue from distillation of Boghead coal in smelting roasted lead-ores.
1859	Bronac and De Herrypon	Employment of spongy iron, prepared at a low temperature.

Patents for Improvements in Separating Silver from Lead or Lead-ores.

Date.	Patentee.	Object of Patent.
1788	Bernie . . .	Treatment of leads by partial calcination and subsequent fusion, with a view to concentrate the silver in the unoxidised portion, utilising the litharge in preparing soda from common salt, and afterwards reducing the oxychloride produced, with lime or carbonate of lime and coal.
1833	Pattinson . . .	The well-known process for separating the lead by crystallisation.
1835	Michell . . .	Fusion of argentiferous ores, either naturally free from sulphur, or freed from it by calcination, with a sulphide, and obtaining the silver concentrated in the regulus.
1838	Chisholm and Bellemois	Conversion of the alloy into litharge, solution of the litharge in acetic acid or acetate of lead, for manufacture of white lead, the silver being obtained in the undissolved residue.
1840	Todd	Melting the ores, and, while melted, running them into a lead-bath, with a view to alloying the silver with the lead.
1843	Neville . . .	Employment of a bath of red-hot lead to extract silver from copper.
1850	Gurlt	Treatment of argentiferous sulphides by a solution of an alkaline chloride in conjunction with chloride of iron, copper, zinc, &c.
1850 1851	Parkes	Separation of the silver from lead by addition of zinc, in combination with which, and with a little lead, it rises to the surface and is skimmed off. Treatment of this alloy by a sort of eliquation to remove part of the lead; separation of the zinc from the remainder by distillation, or by roasting and dissolving out the oxide of zinc with dilute acids. The lead and silver to be then cupelled as usual. The bulk of desilverised lead to be freed from zinc by oxidation at a dull red heat and skimming.
1852	Parkes . . .	Application of the process by zinc, patented by him, to the separation of gold from leads. Also the use of lead or zinc in a state of fusion as a substitute for mercury in extracting silver from ores.
1860	Worsley . . .	Substituting, in Pattinson's crystallising process, a tap-hole by which the rich alloy is run off through a perforated plate, for the ladle by which the crystals are ordinarily removed.

Patents for Improvements in Calcining Hard Lead,

1816	Hall	Calcining hard leads as in the manufacture of red lead, and stopping the process at the point when the remaining lead has become soft.
1854	Pontifex and Glassford	1. Employment of soda, ash, and lime in "improving" hard lead, with the addition of nitre, if the antimony exceed 3 per cent.—2. Reduction of the dross to metal, and separation of the lead and antimony, by a process similar to Pattinson's desilverising method, where the antimony does not exceed 15 per cent. Or, where much antimony is present, washing the dross, treating the residue with acid to remove lead, and reducing the oxide of antimony.
1860	Warner . . .	A method of introducing reagents, as nitre, into a charge of melted lead, by enclosing it in a box.
1860	Baker	Use of alkaline nitrates or chlorates, hypochlorites of alkalis or alkaline earths, sulphate of iron, or bisulphate of potash mixed with common salt, as oxidising agents in improving. And distinguishes

Patents for Improvements in Calcining Hard Lead—continued

Date.	Patentee.	Object of Patent.
		this from similar applications of the above, as being effected in a crucible.
1861	Zenner . . .	Use of oxygen, chlorine, bromine, iodine, or fluorine, either uncombined or in a state of combination, and whether pure or mixed with air or other gases.
		Condensation of Lead Fumes.
1823	Neville . . .	Conveying the fumes by a fan-blast into chambers, which may be kept cool by covering the upper part with water, or into which fluids may be showered.
1825	Broadmeadow .	Not admitting of description apart from drawings.
1841	Lejeune	"The principles which I apply are:—1. The passage under water of vapour separated or mixed with the smoke of fire-places.—2. The use of a vapour-spout as a means of suction.—3. The action of currents on each other and on the surrounding air.—4. A close furnace for the operations of roasting, boiling, sublimating, gassification, &c.—5. The decomposition of sulphurous acid by sulphuretted hydrogen.—6. A furnace with winding chimneys, alternately shut and open."
1843	De Boussois . .	Passing the gases through a series of chambers, and finally forcing through water.
1846	Watson . . .	A partitioned chamber in which the fumes are drawn through water, by the draught created by a peculiarly arranged steam-jet.
1848	Richardson . .	Injection of steam into flue between furnace and chimney, the fumes to pass afterwards into a chamber where they meet a shower of water, further divided by falling on broken bricks, coke, &c., the process being assisted, if necessary, by a steam-jet, as described by Watson.
1848	Lillie	Certain arrangements for distributing condensing liquid in showers by means of centrifugal force, &c.
1848	Young and Young	An arrangement for creating a regulated draught, bringing the particles in contact with the surface of a vessel of water, afterwards injecting steam, if necessary; the steam and particles pass through a series of chambers, and are finally discharged under the fire-grate.
1850	Rodham and Hedley	An arrangement of revolving fans and blades in conjunction with a stream or streams of water to wash the fumes, and pits or hollows to receive and collect the sediment.
1850	Bellford . . .	Passing the gases through showers of purifying liquids produced by means of revolving agitators armed with brushes.
1854	Chapin . . .	Action of jets or showers of water on smoke, &c.
1856	Atkinson . . .	Fans working in connection with a cistern partly filled with water, and divided by perforated floors or wire-gauze partitions.
1857	Parry	Use of perforated disks, &c., which are either alternately immersed in and withdrawn from a fluid, so presenting it in a film to the gases, or, being permanently immersed, serve to promote its contact with the fumes as the latter are forced through.
1858	Jenkins . . .	Condensing lead fume by causing it to come in contact with water before reaching the chimney.
1859	Courage . . .	Steam thrown into flue, also raising the steam by placing water-tanks in flues.
1861	Smith and Bennetts	Employing a fan to force the smoke, &c., through a series of chambers.

N.B.—Many of these patents are intended, not only for lead fume, but for analogous substances and purposes generally.

Other Patents relating to Lead.

Date.	Patentee.	Object of Patent.
1839	Pattinson and Losh	Dissolving galena in hydrochloric acid, and precipitating oxide of lead by an alkaline earth; the oxide to be smelted in the usual way.
1847	Johnson . . .	Extraction of lead from cupel-bottoms by acetic acid or caustic potash.
1848	Parkes. . . .	Coating iron and steel with an alloy of lead and antimony, or lead, antimony, and tin.
1852	Richardson . .	Extraction of the lead from "improving" oxides by acetic acid or nitric acid, the oxide of antimony being left.
1859	Emerson . . .	Decomposition of mendipite, oxysalts of lead, &c., by caustic alkali, to produce an oxide for acetate of lead manufacture.

T. R.

LEAD, ALLOYS OF. Lead forms alloys with several metals by simple fusion, and many of these alloys are definite chemical compounds, which produce mechanical mixtures when fused with either of the constituents in excess. This latter fact has given rise to the metallurgical operation of eliquation.

1. With Antimony.—Lead alloys itself with this metal in several proportions, and the alloys are harder, more tender, and oxidise more easily than lead.

The characteristic action of the antimony is to render the alloy more fusible, as well as harder than either metal.

An alloy of equal parts of the two metals is porous and brittle: 2 pts. of antimony with 1 pt. of lead produce a very hard alloy, capable of receiving a fine polish, and used to make the keys of wind instruments; 3 pts., and even 4 pts. of antimony to 1 pt. of lead produces a hard but malleable alloy.

An alloy of lead and antimony is used in making *type-metal*, a little zinc being sometimes added. Some type-founders add ¾ pt. of tin, but this addition is only suitable for stereotype plates. The plate on which music is printed is composed of:

Tin	12 pts.
Lead	7 pts.
Antimony	1 pt.

The ordinary composition of type-metal is:

Lead	83 pts.
Antimony	17 pts.

When this alloy is heated in the air, the antimony is oxidised more rapidly, and at a lower temperature than the lead, but the oxide which is obtained always contains a large percentage of oxide of lead.

Emery wheels and grinding tools for the lapidary are formed of an alloy of antimony and lead.

Mr. Jas. Nasmyth has suggested the use of lead as a substitute for all works of art hitherto executed in bronze or marble. He states that the addition of 5 per cent. of antimony gives it not only hardness, but greater capability to run into the most delicate parts of the work.

An alloy of this description, analysed by Karsten, and corresponding with the formula $Pb^{18}Sb$, or $Ppb^{9}Sb$, was found on the hearth of a smelting furnace at the Mulder Works:

Lead	90·10
Antimony	6·48
Zinc	1·42
Cadmium	1·50
Silver	0·24
Nickel, arsenic, and sulphur . .	traces
	99·74

2. With Arsenic.—The presence of this substance renders lead brittle, greyish white, and very fusible. The application of heat expels a portion of the arsenic, but the remainder resists the highest temperature.

This alloy constitutes the metal of which shot are cast, 40 lbs. of metallic arsenic being mixed with 20 cwt. of lead.

It also exists native at Clausthal in the Hartz, and is composed of:

Lead	67·63
Arsenic	24·19
Arsenical Pyrites	4·41
Iron	2·26
Sulphur	0·54
Cobalt	0·97
	100·00

3. **With Bismuth.**—This metal unites with lead in all proportions, with condensation. Some of the alloys are more malleable than lead, but the malleability diminishes as soon as the quantity of bismuth equals that of the lead.

When 3 at. lead are united to 2 at. bismuth, the mixture has only one solidifying point, viz. 129° C., but in Pb^2Bi, this point is 146° C.; in PbBi it is 143°, and with Pb^3Bi the temperature is between 163° and 171°.

The influence of the bismuth in these alloys is seen from the following table, in which the numbers in the first and second columns indicate parts by weight:

Alloy.		Properties.
Lead.	Bismuth.	
1	1	Brittle laminar fracture; colour of bismuth; does not expand on cooling.
1	2	Fracture crystalline and coarse-grained; does not perceptibly expand on solidifying.
1	3	Fracture laminar; expands slightly on cooling.
1	8	Coarsely laminar; colour of antimony; expands on cooling.

These alloys have no special application in the arts, but they are used to adulterate mercury. An alloy of 1 pt. lead, 1 pt. bismuth, and 3 pts. mercury, is really an amalgam which is sufficiently fluid to pass through chamois leather. The pure mercury is readily distinguished from the adulterated by the property of the former when poured on a level surface, to run together into one mass, while the latter has no such tendency.

An amalgam of 2 pts. bismuth, 4 pts. lead, and 1 pt. mercury, is solid in the cold, but when pieces of it are rubbed together, they immediately melt.

Lead and bismuth occur associated in nature, in the mineral *Kobellite*, already described (p. 448).

4. **With Bismuth and Antimony.**—When antimony is added to the previous alloy in quantity equal to the bismuth, a metal is obtained which expands on cooling. Advantage is taken of this in casting stereotype plates. This alloy has the following composition, according to Mackenzie:

Lead	9	or	70
Antimony	2	„	15
Bismuth	2	„	15
			100

5. **With Chromium.**—The alloy which contains 0·25 of chromium is fusible at 150° C., ashy-grey, but whiter than lead. It can be hammered into thin sheets, which are very brittle. Nitric acid dissolves the lead without attacking the chromium.

6. **With Copper.**—The alloys of lead and copper are difficult to prepare and to preserve at a high temperature. The copper must be introduced into a bath of lead heated above redness, and the alloy rapidly cooled; even then some portions are reddish-coloured, indicating the commencement of a disunion of the elements. If the alloy is heated to the melting point of lead, the latter abandons the copper, which is left in the form of a porous mass.

The process of eliquation is founded upon this fact, and as the silver present in the copper has a great affinity for the lead, the latter carries off the silver, which is separated in the manner already described (ii. 32).

In smelting sulphide of copper containing sulphide of lead, the latter metal passes off in great measure in the scoriæ in the first operations, but is found in the copper of the subsequent treatment.

There would appear to be two alloys of these metals, one containing more copper, and melting at a higher point than the other, which contains more lead.

Small quantities of lead diminish the ductility of copper at ordinary temperatures, and at a red heat. Copper containing even 0·1 per cent. of lead, may still be used for ordinary purposes, but it cannot be formed into thin sheets or wire.

The alloy of 4 pts. of lead to 1 pt. of copper is employed for casting large movable types.

7. With Manganese.—When a mixture of 892 pts. of protoxide of manganese and 2789 pts. of litharge are heated with a little charcoal in a charcoal-lined crucible, a homogeneous, compact, and ductile alloy is obtained, which can be rolled into thin sheets of great lustre.

8. With Mercury.—This metal is easily alloyed with lead, either by introducing the former into the latter in a melted state, or by triturating lead filings with the mercury.

The amalgam possesses a brilliant white colour, and still remains liquid even with as much as 33 per cent. of lead, but it soils the fingers. The amalgam of equal parts can be crystallised, and a piece of lead plunged into this amalgam is found covered with crystals when it is withdrawn.

The amalgam has a higher specific gravity than either of the metals, owing to the contraction which they undergo in combining.

The presence of 0·0002 to 0·00025 of lead improves the mercury for use in barometers and thermometers, as the latter metal has then not so great a tendency to form globules on the convex surface of the glass.

9. With Mercury and Antimony.—Wetterstedt has found that the addition of a small quantity of mercury to the alloy of antimony and lead removes the tendency of this metal to oxidation. He has proposed to use the triple alloy as a sheathing for ships. It is composed of 94·4 per cent. lead, 4·3 antimony, and 1·3 mercury, and is said not to be so rapidly encrusted with barnacles, &c. as copper sheathing.

10. With Potassium and Sodium.—The alloys of lead with these metals are formed when a reducing alkaline flux is fused with oxide of lead, as first noticed by Vauquelin; and Serullas has described the properties of one of these alloys, obtained when 100 pts. of litharge are strongly heated with 60 pts. of cream of tartar. The alloys can also be prepared directly; that containing 25 per cent. of its volume of potassium is brittle, with a coarse-grained fracture. A similar alloy with sodium is bluish and malleable, but that with one-third of sodium is brittle. These alloys, distilled with the iodides of ethyl, methyl, &c., yield the lead-compounds of the alcohol-radicles. (See LEAD-RADICLES, ORGANIC, p. 560.)

11. With Tin.—Lead may be fused with this metal in all proportions, but the density of the resulting mixtures does not correspond with the specific gravities of the two metals. The following table contains the results of Kupffer's experiments:—

Composition of the Alloys.	Specific Gravity.			Melting Point.
	Found.	Calculated.	Difference.	
Lead, pure	11·3803	. .	. .	335°
Tin, pure	7·2911	. .	. .	230
$SnPpb$*	9·4263	9·4366	0·0103	241
$SnPpb^2$	10·0782	10·0936	0·0154	
$SnPpb^3$	10·3868	10·4122	0·0254	239
$SnPpb^4$	10·5551	10·6002	0·0431	
$PpbSn^2$	8·7454	8·7518	0·0064	196
$PpbSn^3$	8·2914	8·3983	0·0069	186
$PpbSn^4$	8·1730	8·1516	0·0096	189
$PpbSn^5$	8·0279	8·0372	0·0093	194
$PpbSn^6$	7·9210	7·9526	0·0116	

The lead, so soft in itself, has the singular property of increasing the hardness of the tin: it slightly darkens the colour, gives a grained fracture, and causes the peculiar creaking sound, produced on bending tin, to disappear.

The alloys of lead and tin are distinguished by the facility with which they ignite and burn. The alloy of 4 or 5 pts. of lead and 1 pt. tin burns like charcoal at a red heat, the combustion continuing like that of an inferior peat, with the formation of cauliflower excrescences. This action appears to be due to the affinity which exists between the two oxides. The oxides so formed, when fused either alone or with silica and an alkali, produce a white opaque *enamel* used for *dial-plates*, &c., and also in earthenware.

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* Sn = 118 : Ppb = 207.

The *solders* used by plumbers vary much in composition, but there are three commonly known as *fine solder*, composed of 2 pts. of tin and 1 pt. of lead; *common solder*, containing equal pts. of each metal; and *coarse solder*, composed of 2 pts. of lead to 1 pt. of tin. Tomlinson gives the following table of the composition of these alloys and their melting points:—

	Tin.	Lead.	Melting Point.		Tin.	Lead.	Melting Point.
No. 1.	1	25	558°	No. 7.	1½	1	334°
„ 2.	1	10	541	„ 8.	2	1	340
„ 3.	1	5	511	„ 9.	3	1	356
„ 4.	1	3	482	„ 10.	4	1	365
„ 5.	1	2	441	„ 11.	5	1	378
„ 6.	1	1	370	„ 12.	6	1	381

No. 5 is also called plumber's *sealed solder*, which is assayed in the same way as pewter, and then stamped by the officer of the Plumbers' Company. No. 8 is used for soldering cast iron and steel, sal-ammoniac or common resin being used as flux. This alloy is also used for tinned iron, with chloride of zinc or resin as the flux. Gold and silver are also soldered with No. 8, and Venice turpentine for a flux. The same alloy is used with copper, brass, gilding metal, gun metal, &c., and sal-ammoniac, chloride of zinc, or resin as the flux; with zinc, and chloride of zinc as flux; with lead and tin pipes, with a mixture of sweet oil and resin as flux; with Britannia metal, and chloride of zinc or resin as flux. The alloys 4 to 8 are used for ordinary plumber's work, with tallow as flux.

Pewter is another alloy of these metals, and the trade in this article is so important in this country, that the pewterers have formed an incorporated company ever since 1474.

Common pewter is composed of 80 pts. of lead and 20 pts of tin, but other metals are sometimes added, such as copper, antimony, and zinc. The manufacturers of pewter state that a better pewter is obtained by working up old pewter with fresh ingredients.

Holtzapfel gives the following account of these alloys:—"Some pewters are now made as nearly as common as that of equal parts of the metals: when cast they are black, shining, and soft; when turned, dark and bluish. Other pewters only contain ⅕ or ⅙ of lead; these, when cast, are white, without gloss, and hard; such are pronounced very good metal, and are but little darker than tin. The French legislature sanctions the employment of 18 per cent. of lead with 82 per cent. of tin, as quite harmless in vessels for wine and vinegar. The finest pewter, frequently called *tin and temper*, consists mostly of tin, with a very little copper, which makes it hard and somewhat sonorous, but the pewter becomes brown-coloured when the copper is in excess. The copper is melted, and twice its weight of tin is added to it, and from about ½ to 7lbs. of this alloy, or the *temper*, are added to every block of tin weighing from 360 to 390lbs. Antimony is said to harden tin, and to preserve a more silvery colour, but is little used in pewter. Zinc is employed to cleanse the metal, rather than as an ingredient. Some stir the fluid pewter with a thin strip, half zinc and half tin; others allow a small lump of zinc to float on the surface of the fluid metal, while they are casting, to lessen the oxidation."

Plate pewter is the hardest, and is used for making plates and dishes. The pewter called *trifle* is used for beer-pots, and *ley* for the larger wine measures.

Pewter wares are formed either by hammering or by casting, plates and dishes being hammered, while measures and spoons are cast. Pewter is also made in the form of sheets for engraving cheap music, the softness of the metal allowing the notes to be formed by means of punches, instead of engraving with a burin.

Lapidaries, jewellers, and watchmakers use laps and polishers of pewter.

Although lead is so poisonous a metal, it can be employed in domestic utensils, when alloyed with tin, which would appear to neutralise this action of the lead. In an alloy of 3 pts. of lead and 1 pt. of tin, Proust and other chemists have found that vinegar dissolves out nothing but the tin; but for domestic utensils, Vauquelin has shown that the lead ought not to exceed 17 or 18 per cent. An alloy of 3 pts. of lead and 5 pts. of tin is used for tinning certain articles of copper.

The *brilliants of Fahlun* are made with an alloy of 19 pts. of lead and 29 pts. of tin, which are fused together and allowed to cool for a short time. At this point the alloy adheres to a glass tube cut into facets, on which it is allowed to solidify, and from which it can afterwards be easily removed. A lens plunged into this alloy forms a brilliant mirror.

These alloys form superior baths in which to temper various articles of steel; the following table contains all the information on the subject:—

Alloy.		Temperature.		Objects to be tempered.
Lead.	Tin.	C.	F.	
14	8	213·4°	415·4°	Lancets.
15	8	221	429·8	Other surgical instruments.
16	8	225	437	Razors.
17	8	240	464	Penknives, scalpels, cold-chisels.
28	8	257	494·6	Shears, gardeners' tools.
38	8	262	503·6	Hatchets, axes, planes, dressmakers' scissors.
60	8	275	527	Table-knives, large scissors.
96	8	284	543·2	Swords, watch-springs, &c.
100	8	289	552·2	Strong springs, poniards, augers, small saws, &c.

For higher temperatures recourse must be had to other baths.

Alloys of lead and tin are also employed in making anatomical injections.

12. With Tin and Bismuth.—These ternary compounds are well known under the name of *fusible alloys*. They melt at low temperatures, some even below the heat of boiling water. This is one cause why they are so rarely obtained in a perfectly homogeneous condition.

There are several of these alloys known by the name of the first observer; thus, the following all melt below the boiling point of water:

Observer.	Lead.	Bismuth.	Tin.	Melting point.
Homberg . . .	1	1	1	122·00 C.
Rose . . .	1	2	1	93·75
Newton . . .	5	8	3	94·44
Lichtenberg . .	2	5	3	
Krafft . . .	2	5	1	104·00

In whatever proportions the three metals are mixed, they exhibit one fixed solidifying point, at 98° C., and two higher points which are variable.

When 120 lbs. of an alloy, consisting of 3 pts. tin, 2 lead, and 5 bismuth, are melted, they yield, on cooling, tolerably definite crystals, which melt below 100° C., and contain nearly equal numbers of atoms of the three metals, or 15·76 per cent. tin, 26·56 lead, and 57·68 bismuth.

The melting point of fusible metal is raised by the addition of potassium.

This alloy presents many anomalies in its dilatation and contraction; thus, at a temperature from zero up to 35° C., the volume increases in the proportion of 100 : 100·83, and it diminishes up to 56° C. in the ratio of 100·83 : 99·13, which is its point of greatest density; it then begins to expand. It is remarkable that its maximum volume, reached at 35° C. is the same as that which it possesses at 95° C., which is the melting point of Rose's alloy.

It is impossible to determine the melting point of these alloys except by experiment; thus, in Newton's fusible metal, which melts between 198° and 200° F., the theoretical point ought to be 520°, as shown by the calculation,

$$\frac{8\mathrm{Bi} \times 500^\circ + 5\mathrm{Pb} \times 600 + 3\mathrm{Sn} \times 442}{16} = 520^\circ\mathrm{F}.$$

The following table contains the melting points of various alloys of these three metals:

Bismuth.	Lead.	Tin.	Melting point.
8	12	8	130·90° C.
8	5	3	94·44
8	6	3	97.78
8	8	3	109·64
8	8	4	112·20
8	8	6	116·05
8	8	8	122·10°C.
8	10	8	127·60
8	16	8	147·40
8	16	10	149·60
8	16	12	141·90
8	16	14	139·70

Bismuth.	Lead.	Tin.	Melting Point.	Bismuth.	Lead.	Tin.	Melting Point.
8	16	16	140·80° C.	8	28	24	163·00° C.
8	16	18	144·10	8	30	24	170·50
8	16	20	147·40	8	32	24	176·00
8	16	22	152·80	8	32	28	165·00
8	16	24	154·00	8	32	30	163·90
8	18	24	152·90	8	32	32	158·40
8	20	24	151·90	8	32	34	157·30
8	22	24	151·80	8	32	36	158·40
8	24	24	152·90	8	32	38	159·50
8	26	24	158·40	8	32	40	160·60

It is remarkable that the tin, which melts below the fusing points of both lead and bismuth, should raise the melting point of these alloys.

These alloys are of great value in regulating the tempering of delicate articles of cutlery. They are also used for taking impressions of medals, bas-reliefs, and on the Continent for producing casts of metals by the *cliché* process. They can also be employed to take casts from the surface of wood and embossed paper. Beautiful casts of the internal ear, showing the complexities of its bony cavities, have been made with them; also cake-moulds for the manufacture of toilet soaps.

Two of these alloys are well known in this country under the names of *Britannia metal* and *Queen's metal*. The former is composed of equal parts of brass, tin, antimony and bismuth; the latter of 1 part each of antimony, lead and bismuth, with 9 parts of tin. Both are used for making teapots, spoons, &c.

A safer and better alloy is said to be made by adding to 100 pts. of French pewter, 5 pts. antimony and 5 pts. brass, to harden it.

In Birmingham, teapots, milk-jugs, &c. are made into form by a process called *spinning*, which consists in bringing the sheet of pewter against a rapidly revolving tool, by which, with a little dexterity on the part of the workman, it is gradually fashioned.

13. **With Tin, Mercury, and Bismuth.**—The addition of mercury to the three metals forming the previous alloys renders them much more fusible, and communicates some new properties.

D'Arcet's alloy, similar to Newton's, when amalgamated with mercury, melts at 45° C. This alloy or amalgam is specially valuable in making anatomical preparations. It is introduced into the parts of the body in the liquid state, and allowed to solidify. The flesh and other animal matters are afterwards dissolved and removed by a strong solution of potash.

The interior of glass tubes, globes, &c. are tinned by means of this amalgam, which is poured into the vessel by means of a funnel, in the liquid state, and gently agitated. The surplus is then poured off, and the operation is complete. Glass of different colours is employed, and objects of great beauty are thus easily prepared.

The best compound is composed of 1 pt. lead, 1 tin, 2 bismuth, and 10 mercury. The first three are fused together, and then the mercury is added.

14. **With Tin and Copper.**—An alloy of these metals was used by the Romans for casting statues, &c. It was formed of 67·12 per cent. natural bronze, 22·37 old bronze, 5·25 tin, and 5·26 lead.

Bronze is made of copper and tin, to which some manufacturers add a little lead, and in the analyses of several ancient coins by Phillips, lead appears to have been an important constituent. (See Table, vol. ii. p. 45.)

When lead is mixed with copper in the proportion to 6 to 1, ordinary pot-metal is formed, called *dry pot-metal*, a quality which is characteristic of these alloys.

British bell-metal consists of 5·6 per cent. zinc, 10·1 tin, 4·3 lead, and 80·0 copper.

Biddery ware is made in India by combining 2 pts. of tin, 4 pts. lead, and 16 pts. copper, and is afterwards melted in the proportion of 3 pts. to 16 pts. of zinc.

The other alloys of copper to which small quantities of lead are added are described in another part of this dictionary.

15. **With Zinc.**—This metal communicates hardness to lead, and the property of receiving a fine polish, without diminishing the malleability. The two metals may be fused in any proportion, but the alloys are all decomposed at a white heat, the zinc being volatilised, and carrying off with it large quantities of the lead.

The presence of lead in zinc, however, is said to be injurious to the latter metal when rolled into sheets, diminishing its elasticity and probably its tenacity.

When equal quantities of *lead, zinc*, and *bismuth* are fused, an alloy is obtained which melts in boiling water.

The alloy of *lead*, *tin*, and *zinc*, $ZznSn^9Ppb^2 = ZznSn^3,2PpbSn^3$, has but one solidifying point, viz. at 168° C., but all other alloys have also two higher points, *b* and *c*.

Atoms.			Solidifying points.		
Zinc.	Tin.	Lead.*	*a.*	*b.*	*c.*
3	11	2	168°	. .	182°
1	6	1	168	171°	204
1	9	1	168	178	183
1	9	2	168		
1	12	2	168	. .	178
1	12	3	168	172	
1	18	4	168	172	178
1	21	6	168	. .	175
1	33	10	168	. .	178

T. R.

LEAD, ANTIMONIDE OF. (See p. 532.)

LEAD, ARSENIDE OF. (See p. 532.)

LEAD, BROMIDE OF, $PbBr$ or $PpbBr^2$, is obtained by the same processes as the chloride, which it resembles in crystalline form. It is somewhat less soluble in water, and melts out of contact with air, at about the same temperature as the chloride, to a white horny mass. By fusion, in contact with the air, it is converted into a basic bromide or oxybromide. It unites with the bromides of potassium and sodium, forming crystalline double salts, which, however, are decomposed by water.

Acetobromide of lead, $PbBr.C^2H^3PbO^2$, or *Plumbobromacetin*, $\left.\begin{matrix}C^2H^3O\\Ppb''\end{matrix}\right\}\begin{matrix}O\\Br\end{matrix}$, is obtained like the corresponding chlorine-compound (p. 539), which it resembles in its properties and reactions. (Carius.)

LEAD, BROMOCARBONATE OF. An insoluble compound, produced by boiling together equivalent quantities of bromide and carbonate of lead. It fuses readily, and when further heated gives off carbonic anhydride, and leaves an oxybromide of lead.

A *bromophosphate* and *bromophosphite of lead* may be formed in like manner.

LEAD, CHLORIDE OF. $PbCl$ or $PpbCl^2$, *Magisterium plumbi*, sometimes called *Horn-lead*.—Lead unites but slowly with chlorine, the combination not being attended with visible combustion; it is also but slowly attacked by hydrochloric acid, and only when in contact with the air; on the application of heat, it dissolves slowly, with evolution of hydrogen. The chloride is prepared by boiling the protoxide, or carbonate, or sulphide of lead, with water, into which hydrochloric acid is dropped as long as the resulting chloride of lead continues to dissolve, or by adding hydrochloric acid or chloride of sodium to a concentrated solution of a lead-salt. Chloride of lead has also been found, as a natural product, called cotunnite, in the crater of Vesuvius, after the eruption of 1822, mixed with chloride of sodium, and chloride and sulphate of copper. This native chloride occurs in trimetric crystals, in which $\infty\bar{P} : \infty P = 99° 46'$; $oP : \bar{P}\infty = 149° 14'$; and the ratio of the principal axis, brachydiagonal and macrodiagonal, is as 0·5953 : 1 : 1·1868. The observed planes are ∞P, $\infty\bar{P}\infty$, $\infty\breve{P}\infty$ $2\breve{P}\infty$, $\bar{P}\infty$. Also acicular crystals. It is soft enough to be scratched by the nail, and has a specific gravity of 5·238. Lustre adamantine, inclining to silky or pearly. Colour white. Streak white. (Dana, ii. 97.)

Chloride of lead dissolves in 135 pts. of cold water, in less than 30 pts. of boiling water, and separates from the solution in long, flat, needle-shaped crystals. It dissolves in pure water, and in strong *hydrochloric acid* more easily than in the dilute acid, and therefore separates from the acid solution on moderate dilution with water, and from the saturated aqueous solution, on addition of hydrochloric acid. It is also somewhat soluble in weak alcohol, very sparingly in alcohol of 76 per cent., and insoluble in alcohol of 94 per cent.. Its solubility in water is greatly diminished by the presence of chloride of calcium. In solutions of alkaline hyposulphites, or of acetate of sodium, on the contrary, it is much more soluble than in water, so that, on mixing a solution of 190 pts. acetate of lead with 58·5 pts. chloride of sodium, only 43 to 48 pts. of lead-chloride are precipitated, whereas 139 pts. are formed. A solution of the chloride in strong hydrochloric acid is not precipitated by *sulphydric acid*, but on addition of water, precipitation immediately takes place. A solution of lead-chloride mixed with aqueous sulphydric acid containing hydrochloric acid, forms a yellow or reddish-brown precipitate of sulphochloride of lead (p. 559). An aqueous solution of the chloride mixed with sal-ammoniac is not precipitated by sulphuric acid.

Chloride of lead melts when heated out of contact with air, and may be sublimed, though with difficulty; the fused mass solidifies on cooling, to a white translucent fissured mass of specific gravity 5·8, formerly called horn-lead. When heated in contact with the air, it fumes strongly before the heat rises to redness, then turns yellow, and is converted into an oxychloride (p. 555). When it is heated in a stream of *carbonic oxide*, chloride of carbonyl (phosgene) $COCl^2$, is formed, and metallic lead is separated (Göbel). It quickly absorbs *ammonia-gas*. When it is moderately heated in *phosphoretted hydrogen gas*, hydrochloric acid is given off, phosphorus distils over, and metallic lead remains. A solution of *hypochlorous* acid converts it into peroxide of lead.

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* Atomic weight of zinc = 5; of tin = 118; of lead = 207.

Acetochloride of lead, $PbCl.C^2H^3PbO^2$, or *Plumbochloracetin*, $\left.\begin{matrix} C^2H^3O \\ Ppb'' \end{matrix}\right\}\begin{matrix} O \\ Cl \end{matrix}$, is obtained in monoclinic crystals, by mixing recently precipitated chloride of lead with acetate of lead, and a sufficient quantity of glacial acetic acid, to form a viscid mass, which solidifies in a short time, and either freeing this mass from excess of acetic acid by pressure, or heating it in a sealed tube to 130° or 140°;—or together with acetate of ethyl, by the action of acetate of lead on chloride of ethyl. It dissolves, though with difficulty, in acetic acid without decomposition, but is decomposed by water, with separation of a small quantity of lead-chloride, and formation of the compound $PbCl.3C^2H^3PbO^2$ or $\left.\begin{matrix} (C^2H^3O)^3 \\ \overset{''}{P}pb^2 \end{matrix}\right\}\begin{matrix} O^3 \\ Cl \end{matrix}$, which dissolves in the water, and may be recrystallised without decomposition. It is decomposed, however, by glacial acetic acid, which leaves the original compound. The compound, $\left.\begin{matrix} C^2H^3O \\ Ppb'' \end{matrix}\right\}\begin{matrix} O \\ Cl \end{matrix}$, is analogous to glycolic chloracetin, $\left.\begin{matrix} C^2H^3O \\ (C^2H^4)'' \end{matrix}\right\}\begin{matrix} O \\ Cl \end{matrix}$ (ii. 568), and may therefore be called plumbochloracetin. Its constitution affords an argument in favour of doubling the ordinary atomic weight of lead. (Carius, Ann. Ch. Pharm. cxxvii. 87.)

LEAD, CHLOROCARBONATE OF. $2PbCl.Pb^2CO^3$, or $\left.\begin{matrix} (CO)'' \\ \overset{''}{P}pb^2 \end{matrix}\right\}\begin{matrix} O^3 \\ Cl^2 \end{matrix}$.—This compound is produced as a white insoluble powder, by boiling 1 at. carbonate of lead with 2 at. (or more) of the chloride, and water. It also occurs native, though rarely, as corneous lead or kerasin, in acute quadratic pyramids in which P : P in the lateral edges = 113° 48′, and in the terminal edges = 107° 22′. Observed faces ∞P∞, P, ∞P, P and others. Cleavage distinct parallel to ∞P. The mineral likewise occurs in botryoïdal and stalactitic forms. Hardness = 2·5 to 3·0. Specific gravity = 6·0 to 6·1. Colour white, grey, and yellow. Streak white. Transparent to translucent. Fracture conchoïdal. Rather sectile. It occurs at Crawford, near Matlock in Derbyshire, in minute crystals at a lead mine near Elgin in Scotland, and at Tarnowitz, in Upper Silesia, where also large pseudomorphs of lead-carbonate (cerusite) in the form of this mineral are found.

Both the natural and the artificial compound fuse readily, and are converted at a higher temperature, with loss of 7·5 per cent. CO^2, into the oxychloride, $2PbCl.Pb^2O$.

LEAD, CHLORIODIDE OF. Obtained in pale yellow four-sided needles, from a solution of the iodide in boiling hydrochloric acid; it is gradually decomposed by water, which extracts the chloride of lead. (Labouré, J. Pharm. [3] iv. 328.)

LEAD, CHLOROFLUORIDE OF. Pb^2ClF, or $PpbClF$.—Formed by precipitating aqueous fluoride of sodium with a boiling solution of chloride of lead, or with a mixture of acetate of lead and chloride of sodium. It is a white powder, which melts when heated, without giving off water or acid. Dissolves in water without decomposition, and easily in nitric acid. (Berzelius.)

LEAD, CHLOROPHOSPHATE OF. When a boiling solution of chloride of lead is poured into a boiling solution of phosphate of sodium, the latter being in excess, a precipitate containing $2(PbCl.3Pb^3PO^4).H^2O$ is formed, insoluble in water, but soluble in nitric acid, which converts it into a nitrophosphate. (Heintz, Pogg. Ann. lxxiii. 122). When, on the contrary, a boiling solution of phosphate of sodium is poured into an excess of chloride of lead, a precipitate is formed which, according to Heintz, is composed of $PbCl.2Pb^3PO^4$, but according to Gerhardt (Ann. Ch. Phys. [3] xxii. 505), of $PbCl.Pb^2HPO^4$. The same compound is formed when a soluble phosphate is precipitated by a lead-solution in presence of a soluble chloride.

The compound $PbCl.3Pb^3PbO^4$ occurs native as pyromorphite, sometimes pure, sometimes having part of the phosphorus replaced by arsenic, sometimes associated with fluoride and phosphate of calcium. (See PYROMORPHITE.)

LEAD, CHLOROPHOSPHITE OF. Lead-salts added to a solution of alkaline phosphite, obtained by dissolving trichloride of phosphorus in water, and neutralising with an alkali, throw down a precipitate containing a compound of chloride and phosphite of lead, from which boiling water extracts the former.

LEAD, DETECTION AND ESTIMATION OF. I. *Reactions in the dry way.*—Lead-salts heated on charcoal with carbonate of sodium or cyanide of potassium, give, in the inner blowpipe flame, bluish-white, malleable beads of metallic lead, surrounded by an incrustation of oxide, brownish-yellow while hot, but light lemon-yellow on cooling. Added, in rather large quantity, to a bead of microcosmic salt, they give on cooling, a bead having an enamel-white colour, or yellow if quite saturated.

II. *Reactions in Solutions.*

Soluble lead-salts are colourless; the metal is precipitated from their solutions by *zinc* or *iron*.

Sulphydric acid and *alkaline sulphides* throw down sulphide of lead as a black or brownish-black precipitate, insoluble in cold and dilute solutions of acids, alkalis, and alkaline sulphides. In extremely dilute solutions, only a brown colouring is produced. If the solution of the lead-salt contains free hydrochloric acid, the precipitate is red or yellow, and a large excess of hydrochloric acid prevents it altogether.

Hydrochloric acid, added to solutions not too dilute, throws down chloride of lead, as a white precipitate, slightly soluble in cold water, but more so in boiling water, deposited in needles on cooling; less soluble in dilute hydrochloric acid than in water, but pretty freely in the strong acid; apparently unaffected by ammonia, but rendered insoluble in water, from conversion into oxychloride.

Sulphuric acid and *soluble sulphates* throw down sulphate of lead as a white precipitate, scarcely soluble in cold water, ($\frac{1}{22,800}$ Fresenius), and in dilute sulphuric acid ($\frac{1}{36,500}$ Fresenius), almost absolutely insoluble in alcohol; soluble in strong hydrochloric acid on heating; in nitric acid more readily when strong and hot; in concentrated sulphuric acid, slightly; in ammoniacal salts, more especially the acetate.

Caustic potash or *soda* throws down the hydrate of lead as a white precipitate, soluble in acids, or in excess of the reagent.

Ammonia throws down a white precipitate of basic lead-salt, insoluble in excess.

Chromate of potassium throws down chromate of lead as a yellow precipitate, insoluble in water (slightly soluble in excess, according to Conybeare), soluble in potash, insoluble in dilute nitric acid, converted by ammonia into a red basic chromate.

Iodide of potassium produces a bright yellow precipitate of iodide of lead, which dissolves in *boiling* water, and separates on cooling in crystalline spangles, exhibiting a beautiful play of colours.

LIMITS OF REACTIONS OF TESTS FOR LEAD.

One part of	In water,	Reagent.	Authority.
Lead . . .	100,000 or more.	Sulphydric acid.	A. S. Taylor.
Lead, as nitrate .	200,000	"	Lassaigne.
Oxide of lead, as do. .	350,000	"	Harting.
Nitrate of lead .	100,000	"	Pfaff.
Oxide, as nitrate .	20,000	Sulphuric acid in exc.	Pfaff and Harting.
Lead, " .	25,000	Sulphate of sodium (in 15 minutes).	Lassaigne.
Oxide, " .	70,000	Chromate of potassium.	Harting.

The reactions with sulphydric, sulphuric and hydrochloric acids, taken together, serve to distinguish lead from all other metals. The reactions with iodide and chromate of potassium are also very characteristic.

III. *Quantitative Estimation.*

1. *Gravimetric methods.*—Lead is generally most conveniently estimated as sulphate. The concentrated solution is mixed with a slight excess of *dilute sulphuric acid* and about twice its volume of alcohol, filtered after a few hours, the precipitate then washed with alcohol, and dried, and the filter burnt off. Or, a considerable amount of sulphuric acid may be substituted for the alcohol, in which case the wash-waters must be also acidulated with sulphuric acid, and the last washings displaced by alcohol. In burning off, as much of the precipitate as possible is to be detached from the filter, which should be burnt separately, to guard against reduction of lead. In all cases it is safest to employ a porcelain crucible.

2. Lead may also be weighed as oxide, into which it may be converted directly by ignition, or after previous precipitation as oxalate or carbonate (results low), or as chromate on a tared filter.

Volumetric methods.—Many methods have been proposed for the volumetric estimation of lead, but the greater number give only approximate results. 1. **Flores Domonte** adds to the lead-solution a quantity of caustic potash or soda sufficient to redissolve the lead-oxide at first precipitated, and then adds to the boiling liquid from a burette, a graduated solution of *sulphide of sodium* as long as a precipitate is thereby produced. The greater part of the sulphide of lead cakes together, but the liquid remains brownish, so that it is difficult to see when the precipitation is complete. The method is, however, useful for technical purposes. The strength of the solution of sulphide of sodium must be determined every two days.

2. **Margueritte** adds to an alkaline lead-solution, a graduated solution of *permanganate of potassium*, which throws down the peroxides of lead and manganese, continuing the addition till the liquid exhibits a permanent green colour. The solution bumps very strongly when boiled, and the ready alterability of the solution of the permanganate necessitates frequent titration.

3. **Pappenheim**, according to **Mohr**, adds to the lead-solution a graduated solution of *sulphate of potassium*, till the liquid no longer produces a yellow spot of iodide of lead on paper prepared with solution of iodide of potassium. This method yields nearly exact results.

4. **Streng** (Ann. Ch. Pharm. xcii. 413) supersaturates a solution of a lead-salt, or sulphate of lead suspended in water, with potash; adds an excess of solution of *chloride of lime*, and boils for a while, whereby the lead is entirely converted into peroxide. The precipitate is collected on a filter and washed with hot water; a hole is then made in the bottom of the filter, and the precipitate washed through into the vessel in which it was formed; solution of *stannous chloride* is passed through the filter from a burette till all the peroxide of lead is washed off; the filter is again washed with hot water; and an excess of the tin-solution is added, whereby the peroxide of lead is converted into chloride, which is then dissolved by heating it with water and hydrochloric acid. If the excess of *stannous chloride* in the liquid be then determined by means of a standard solution of chromate of potassium, the whole of the data for calculating the amount of lead present in the liquid under examination will be obtained. This method is exact and often convenient.

5. The following process, given by **Hempel** (Jahresber. 1853, p. 627), is, however, simpler, and has the advantage of admitting of a double verification. The lead is precipitated with a measured quantity of a graduated solution of *oxalic acid* added in excess; the liquid is neutralised with ammonia, and the precipitate collected on a filter; the amount of oxalic acid in the filtrate is then determined by means of a standard solution of *permanganate of potassium*, and by deducting this amount from the total quantity of oxalic acid used, the quantity of oxalic acid combined with the lead is found, and thence the amount of the lead may be calculated.

The result may be checked, either by digesting the precipitate in dilute sulphuric acid, which sets the oxalic acid free, and estimating the amount of oxalic acid in the filtrate with a solution of permanganate — or by igniting and weighing the precipitate.

Mohr completes the determination without filtration. He adds to the solution, in a flask holding 300 cubic centimetres, a drop of tincture of litmus; then adds, from a burette, a standard solution of oxalic acid as long as a white precipitate is formed; saturates with ammonia till the liquid turns blue; fills the flask with water; leaves the liquid to stand for about half an hour till it is sufficiently clarified to allow of 100 cubic centimetres being removed clear with the pipette; and determines the free oxalic acid therein by means of a solution of permanganate, the quantity of which, multiplied by 3, gives the data required for determining the quantity of oxalic acid added in excess. It appears, however, that a small quantity of nitrate of lead is always precipitated together with the oxalate, so that the quantity of oxalic acid used always appears too small. Mohr estimates the errors thence arising at 2 per cent. (Handw. d. Chem. 2te Aufl. ii. [2] 33). On the whole, the volumetric methods of estimating lead do not appear to be so advantageous as the gravimetric methods.

IV. *Separation of Lead from other Metals.*

From all metals, not precipitable as sulphides in acid-solution, lead may be separated, by passing *sulphydric acid gas* to saturation through the solution, previously made moderately acid with hydrochloric or nitric acid. The solution should also be moderately dilute. If no other metal, precipitable by the gas, be present, the precipitate will be sulphide of lead with an uncertain quantity of sulphur. If this is deflagrated with nitre, and the sulphur estimated as sulphate of barium, the difference between its weight and that of the precipitate, thoroughly dried at 100°, will give the lead. Or, by oxidising the precipitate in a porcelain vessel with fuming nitric acid, after detaching it as much as possible from the filter, burning the filter, and adding the ash, we obtain a mixture of sulphate of lead with a little nitrate. This may be converted into sulphate by a slight excess of pure concentrated sulphuric acid; the precipitate is then ignited and weighed, and the lead calculated therefrom.

Of the metals precipitable by sulphydric acid, gold, platinum, arsenic, tin, and antimony may be further separated by digestion of the mixed sulphides in sulphide of ammonium containing an excess of sulphur. If, after this treatment, any silver, mercury, bismuth, cadmium, or copper be left with the lead-sulphide, they may be separated by one of the two following methods:—

If no bismuth is present, the solution containing the mixed oxides, is treated with *carbonate of sodium*, and then digested with *cyanide of potassium*, when, on filtering, carbonate of lead will remain alone on the filter.

From bismuth, the lead may be separated by the following method, applicable also to its isolation from mercury, copper, and cadmium, but not from silver, if present in any quantity:—Evaporate with excess of sulphuric acid until fumes of acid appear, cool, and dilute with water; filter at once from the sulphate of lead; wash with acidulated water and alcohol; then dry and weigh.

The method of precipitation by sulphuric acid, or a soluble sulphate, serves, indeed, to separate lead in solution without any preliminary treatment, from all metals, excepting barium, strontium, and calcium (and perhaps silver, *vid. sup.*), and from these earth-metals it is easily separated by sulphydric acid.

In alloys, lead may be very conveniently separated from bismuth, tin, and antimony, and with rather more difficulty from arsenic, by converting all the metals into sulphides, and heating the sulphides in a stream of dry *chlorine gas;* all the other metals will then be volatilised, the lead alone remaining.

V. *Valuation of Lead Ores.*

a. By the wet way.—A very convenient process for determining lead in ores, especially in galena, consists in oxidising them with fuming nitric acid, adding sulphuric acid in considerable excess to the slightly diluted solution, filtering and washing the residue, as before directed, and after weighing, boiling it repeatedly with a strong solution of acetate of ammonium, which dissolves the lead-sulphate. The insoluble residue deducted from the first weight gives the amount of lead-sulphate, from which the lead may be calculated.

b. By the dry way.—For the purposes of assaying, lead ores may be divided into two principal classes:—

A. Ores &c. which contain no sulphur, arsenic, or phosphorus.
B. Ores containing one or more of the above elements.

A. *First class.*—In the assay of these ores, two points require attention; heating with a reducing agent for the separation of the lead, and with an alkaline flux to facilitate the formation of a clean button. Charcoal and argol are among the best reducing agents; carbonate of sodium, borax, deprived of its water by previous fusion, and salt, are useful as fluxes. Black flux, or a mixture of carbon in a fine state of division with carbonate of potassium, may also be employed. The following mixtures will give some idea of the proportions in which these reagents should be employed, but they must, of course, vary somewhat for different ores:

	Sample.	Argol.	Charcoal.	Carbonate of sodium.	Borax glass.	Salt.
No. 1.	200 gr.	100	. .	300	. .	200–250 grs.
2.	400 „	200	. .	400	200	„
3.	400 „	200	. .	400	200	„
4.	400 „	. .	50–60	600	. .	„
5.	400 „	200	. .	400	. .	„
6.	400 „	600	black flux, and a cover of borax			„

1. Recommended by Mitchell for oxides, carbonates, cupel-products, &c.
2. „ „ cupel-bottoms and other refractory products.
3. „ „ fumes, siliceous slags, &c.

4, 5, 6. Phillips:—The salt is not mixed with the other reagents, but employed to cover the whole mixture.

Ores of this class may also be assayed by the following process, proposed by the writer:—Weigh out 50 grs. of ore on a counterpoise. Fuse, at a red heat, about an ounce of crude cyanide of potassium in a crucible capable of holding at least double the quantity; when fused remove it from the furnace, and add the ore in small portions with a spatula; rinse the last traces off with a little more cyanide, and replace it for a minute or two in the fire, then take out the crucible, and tap to collect the lead into a button.

B. *Second class.*—Galena, pure, and mixed with gangue, is included in this class, for the assay of which several methods, more or less accurate, are employed, as—

1. *Roasting the galena*, by which it is converted into oxide, and treating the product as an ore of the first class. This process, besides being exceedingly troublesome, gives little more than three-fourths of the lead actually present.

2. *Fusion with 3–4 parts of alkaline carbonate;* the mixture to be heated slowly till fused, which gives about 90 per cent. of the lead present.

3. *Fusion with carbonate of sodium and nitre*, by which the sulphur of the ore is removed as sulphate of potassium; if an excess of the nitrate is employed, a portion of the lead is oxidised and lost. Several assays must therefore be made to discover the best proportions. This process answers very well for obtaining a button to be afterwards assayed for silver, in which case a slight excess of nitre must be used to ensure complete oxidation of the sulphur, without which some silver is liable to be retained as sulphide in the slag.

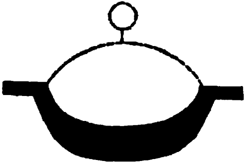
4. *Fusion with metallic iron*, which has been variously modified as to details. The oldest plan is that given by Berthier, in which the galena is simply mixed with about 30 per cent. of finely divided iron, covered with a layer of some flux and heated; it gives an amount of metal 7–10 per cent. below that actually present. Small iron nails are also recommended by Berthier, which is not a satisfactory process, as the nails become fixed in the button. Mitchell suggests the use of tenpenny nails; Phillips, of iron crucibles, and lastly, a mixture of iron-oxide with a reducing flux. Of these different modifications, the process of Mitchell is especially useful on account its simplicity and accuracy. We extract Mr. Mitchell's own description in full:

"To 200 grains of finely pulverised galena add 50 of argol, and 200 carbonate of soda; place the mixture in a crucible, the inside of which has been smeared with black-lead; introduce three tenpenny nails head downwards; tap the crucible on the mixing bench, so that the contents may occupy as little space as may be; cover with about 200 grains of salt, over that 200 grains of borax. Prepare two crucibles thus, place them in the furnace, and raise the heat rapidly to nearly a bright red; uncover the furnace, and allow the crucibles to remain for 8–10 minutes; again cover the furnace and raise to a bright red: the crucibles will then be ready for removal. Besides the time occupied, the termination of the assay may be judged by the flux flowing smoothly. When this occurs, seize hold of the crucible with the large tongs, and with a smaller pair take hold of one of the nails; rinse it well in the flux to remove any small globules of lead; and then reject it. The two other nails are to be treated in the same way, the crucible removed, tapped on the furnace top to collect all globules, and set aside to cool. So also with the second crucible. When cold they are broken, &c., as usual; the assays should correspond within one-eighth of a grain."

The following is an account of the process employed in the lead-works of North and South Wales, as an example of the rougher methods often adopted in smelting works with good practical results.

In the Welsh lead-works, the assays are generally made on 10 ounces of the ore as received, wet or dry. This is melted in a stout iron dish (*fig.* 637) with a cover, in a smithy fire; when melted, the slag is skimmed back and the produce weighed, each ounce representing 10 per cent., and each dwt. ½ per cent. In the assay of galenas, some modification may be required; according to Mitchell, by fusing antimonial galenas with carbonate of sodium, pure lead is obtained, but with black flux, the lead contains much antimony; and if iron, either alone or mixed with black flux, be employed, all the antimony is obtained with the lead; but repeated tentative assays must be made to obtain the best possible result. When a lead ore contains oxidised compounds of sulphur and arsenic, reducers alone will not answer; but if they are mixed with an alkaline carbonate and metallic iron, good results are obtained. The assay may be conducted as in Mitchell's process for galenas.

Fig. 637.



A notable loss of lead is sustained in all the above processes, arising chiefly from the volatility of this metal and its oxide: hence the necessity of making all lead-assays at the lowest temperature compatible with perfect fusion, and of not keeping the assay in the furnace longer than is actually necessary. An error in the opposite direction may arise from the presence of foreign metals in the ore, which are more or less completely reduced and alloyed with the lead, increasing its weight; such, for example, as silver, copper, tin, or antimony. Zinc is completely removed if the heat be sufficient, but it entails a loss of lead. Iron does not go down with the lead, unless the assay be much overheated. The separation of most of these metals from lead, by the dry way, is impracticable, with the exception of silver in argentiferous lead, which will bed escribed under *Cupellation* (see below).

Whatever process is employed to determine the lead, some standard is adopted by the manufacturer, to which to refer in calculating the value of the ores. For example, in Wales the "standard" is 77 per cent. or 7 oz. 14 dwts. on the assay. The value of this standard fluctuates with the market price of lead, and for every variation of a dwt. or half a per cent. an established addition or deduction is made in the price. Any silver present is calculated in ounces on the ton, and paid for per ounce.

The following tables have been constructed to save trouble in calculating the results of assays:—

Produce of Lead per ton of Ore, calculated from Assay.

Per cent.	cwt.	qrs.	lbs.	Per cent.	cwt.	qrs.	lbs.	Per cent.	cwt.	qrs.	lbs.
½	0	0	11	6	1	0	22	30	6	0	0
1	0	0	22	7	1	1	16	40	8	0	0
2	0	1	16	8	1	2	11	50	10	0	0
3	0	2	11	9	1	3	5	60	12	0	0
4	0	3	5	10	2	0	0	70	14	0	0
5	1	0	0	20	4	0	0	80	16	0	0

Produce of Lead per bing of Ore, calculated from Assay.

Per cent.	cwt.	qrs.	lbs.	Per cent.	cwt.	qrs.	lbs.	Per cent.	cwt.	qrs.	lbs.
·10	0	0	·896	1·00	0	0	8·96	10·00	0	3	5·60
·20	0	0	1·792	2·00	0	0	17·92	20·00	1	2	11·20
·30	0	0	2·688	3·00	0	0	26·88	30·00	2	1	16·80
·40	0	0	3·584	4·00	0	1	7·84	40·00	3	0	22·40
·50	0	0	4·480	5·00	0	1	16·80	50·00	4	0	0·
·60	0	0	5·376	6·00	0	1	25·76	60·00	4	3	5·60
·70	0	0	6·272	7·00	0	2	26·72	70·00	5	2	11·20
·80	0	0	7·168	8·00	0	2	15·68	80·00	6	1	16·80
·90	0	0	8·064	9·00	0	2	24·64				

Estimation of the Silver.—The separation of lead and silver in the dry way, by the process known as cupellation, depends on the fact, that while lead, when exposed to the air at temperatures above its melting point, is rapidly oxidised, silver remains unaltered. If, therefore, an argentiferous lead is heated in a current of air, on a support of such a texture that the litharge formed from the lead shall be absorbed as fast as produced, the silver will be finally left in the form of a button. This support is called the "cupel," a flat, slightly hollowed-out dish of pounded bone-ash, compressed by a mould into the proper form. The process is conducted in a furnace, such as is shown in *figs.* 638, 639, where *a* is the ash-pit door; d'' and *f*, doors for supply of fuel; d', the opening by which access is obtained and the supply of air regulated to the muffle *m*. This muffle is a small fire-clay oven, situated in the centre of the fire, and pierced by slits at the sides and inner end, which, when the door is opened, establish a current of air through the apparatus, while it is maintained at any desired temperature by means of a damper. In using the apparatus, the muffle is first raised to a red heat; 4 to 8, or more, well-dried cupels are then introduced, and the door closed. When they have attained a clear red heat, the door is opened, a button of lead is placed in each cupel by tongs, and the door again closed. On opening it partially, the buttons are seen "uncovered," or presenting a bright metallic surface, and a dark ring instantly begins to form round the circumference of the lead, as the litharge formed by its oxidation is absorbed by the cupel, the rings gradually extending as the buttons diminish. The moment when the oxidation is completed and pure silver left, is recognised by a peculiar phenomenon known as the "brightening" of the silver button, which appears, for an instant, to revolve rapidly on its axis, while covered with a play of prismatic colours. The play of colours disappears, and the button becomes still and lustrous. It is then withdrawn from the furnace, detached from the cupel, cleaned, and weighed in a balance turning with ·001 gr. Simple as the process appears, some practice is required, and many points demand attention, before uniform results can be obtained.

The temperature should be the lowest at which the assay will proceed steadily, as a sensible amount of silver is volatilised with the vapour of lead. The temperature, on the other hand, must not be reduced *too* low, as the absorption of the litharge by the cupel is then impeded. Again, the draught, if too rapid, cools the cupel unduly, and if too slow, does not effect the oxidation with sufficient rapidity, thereby increasing the loss by volatilisation. Further, the absolute quantity of silver remaining the same, if the quantity of lead be much increased, the loss in silver will be greater. But, if the silver-lead be very rich, a loss will arise from the absorption of the alloy into the pores of the cupel. When the heat is too great, the cupels are whitish and the metallic matter they contain can scarcely be seen; the fume is scarcely visible, and rises rapidly to the arch of the muffle. When the heat is not strong enough, the smoke is thick and heavy, falling in the muffle, and the litharge can be seen forming lumps and scales about the assay. When the heat is properly managed, the cupel is red, and the fused metal luminous and clear.

Fig. 638.

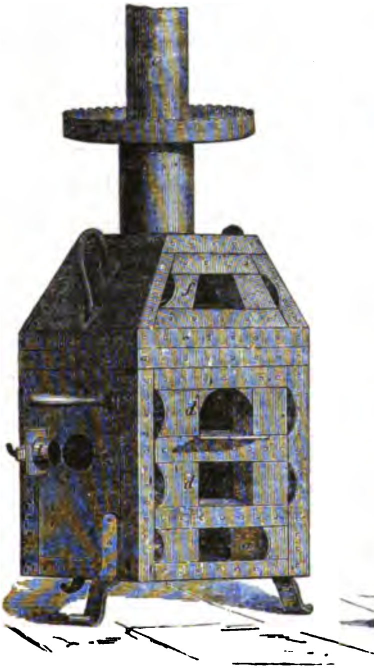
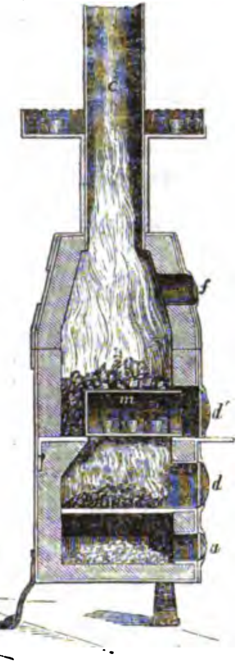


Fig. 639.



Lastly, a source of loss arises from what is termed "vegetation" of the button, which is due to the absorption of oxygen by the molten metal. When the metal is cooling, in a button of any size, the surface cools and solidifies before the centre has abandoned its mechanically dissolved gas, which, when it is liberated, forces its way through the external crust, raising it into fantastic arborescent forms, which, once seen, sufficiently explain the term. But as portions are frequently projected outwards by the sudden action, it is necessary to cover the cupel, while still hot, with a previously heated old cupel to secure its very gradual cooling. It is only, however, in the case of buttons much larger than a pin's head that this precaution is essential. The weight of the cupel ought to be about one-third greater than that of the lead to be cupelled; a good cupel will absorb its own weight of litharge under ordinary circumstances.

Lead is not the only metal which may be separated from silver by this process. Bismuth may be perfectly "cupelled," and copper, antimony, iron, tin, &c., may be "passed" by the addition of sufficient lead to carry their oxides into the cupel.

The following tables are useful in an assay office, where numerous assays are made from time to time, and they are constructed for different weights of lead cupelled, as well as the produce per 20 cwt. or ton and per 21 cwt. or fodder of lead:—

Yield of Silver per ton, calculated from Assay of 400 *grs.*

400 grs. give	Yield per ton. oz.	dwts.	grs.	400 grs. give	Yield per ton. oz.	dwts.	grs.	400 grs. give	Yield per ton. oz.	dwts.	grs.
0·001	0	1	15	0·05	4	1	16	0·8	65	6	16
·002	0	3	6	·06	4	18	0	0·9	73	10	0
·003	0	4	21	·07	5	14	8	1·0	81	13	8
·004	0	6	12	·08	6	10	16	2·0	163	6	16
·005	0	8	4	·09	7	7	0	3·0	245	0	0
·006	0	9	19	·10	8	8	8	4·0	326	13	8
·007	0	11	10	·20	16	6	16	5·0	408	6	16
·008	0	13	1	·30	24	10	0	6·0	490	0	0
·009	0	14	16	·40	32	13	8	7·0	571	13	8
·010	0	16	8	·50	40	16	16	8·0	653	6	16
·020	1	12	16	·60	49	0	0	9·0	735	0	0
·030	2	9	0	·70	57	3	8	10·0	816	13	8
·040	3	5	8								

Yield of Silver per ton, calculated from Assay of 1 *oz.*

1 oz. gives grs.	Yield per ton. oz.	dwts.	grs.	1 oz. gives grs.	Yield per ton. oz.	dwts.	grs.	1 oz. gives grs.	Yield per ton. oz.	dwts.	grs.
0·001	0	1	11·84	0·05	3	14	16·0	0·8	59	14	16·0
·002	0	2	23·68	·06	4	9	14·4	0·9	67	4	0·0
·003	0	4	11·52	·07	5	4	12·8	1·0	74	13	8·0
·004	0	5	23·36	·08	5	19	11·2	2·0	149	6	16·0
·005	0	7	11·20	·09	6	14	9·6	3·0	224	0	0·0
·006	0	8	23·04	·10	7	9	8·0	4·0	298	13	8·0
·007	0	10	10·88	·20	14	18	16·0	5·0	373	6	16·0
·008	0	11	22·72	·30	22	8	0·0	6·0	448	0	0·0
·009	0	13	10·56	·40	29	17	8·0	7·0	522	13	8·0
·010	0	14	22·40	·50	37	6	16·0	8·0	597	6	16·0
·020	1	9	20·80	·60	44	16	0·0	9·0	672	0	0·0
·030	2	4	19·20	·70	52	5	8·0	10·0	746	13	8·0
·040	2	19	17·60								

Table of Silver per Fodder of Lead, calculated from Assay of 1 *oz.*

1 oz. gives grs.	oz.	dwts.	grs.	1 oz. gives grs.	oz.	dwts.	grs.	1 oz. gives grs.	oz.	dwts.	grs.
0·001	0	1	13·6	0·009	0	14	2	0·08	6	5	10
·002	0	3	3·2	·010	0	15	16	·09	7	1	2
·003	0	4	16·0	·020	1	11	8	·10	7	16	9
·004	0	6	6·0	·030	2	7	0	·20	15	13	14
·005	0	7	20·0	·040	3	2	17	·30	23	10	9
·006	0	9	9·0	·050	3	18	9	·40	31	7	4
·007	0	10	23·0	·060	4	14	1	·50	39	4	0
·008	0	12	13·0	·070	5	9	8				

VI. *Atomic Weight of Lead.*

The atomic weight of this metal has been determined chiefly by the experiments of Berzelius, made in 1830 and 1845 (Pogg. Ann. xix. 300; *Lehrbuch*, 5te Aufl. iii. 1187). By reducing pure protoxide of lead with hydrogen gas, he found that 100 pts. of the protoxide contain 7·1724 pts. oxygen, whence, regarding the protoxide as Pb^2O, and putting oxygen = 16, the atomic weight of lead is 103·54; if, however, a certain number of the determinations, which do not agree very well with the rest, be left out of account, the atomic weight is found to be 103·57. The extreme limits of the determinations in question were 103·36 and 103·65. Within the same limits also are comprised the older determinations of Berzelius (1818), which gave 103·56; also those of Turner in 1835 (Ann. Ch. Pharm. xiii. 14), which gave 103·61, and nearly also those of Longchamp in 1827 (Ann. Ch. Phys. [2] xxxiv. 105), which gave numbers ranging from 103·64 to 103·74. The mean of all the best determinations is 103·56; or if lead be regarded as diatomic, and the protoxide be represented by the formula $Ppb''O$, then the atomic weight is 207·12. T. R.

LEAD, FLUORIDE OF, PbF or $PpbF^2$, is obtained by precipitating acetate of lead with hydrofluoric acid, or by decomposing carbonate of lead with the same acid, as a white powder, sparingly soluble in water, easily fusible, soluble in hydrochloric and in nitric acid, by which it is decomposed on evaporation. When treated with aqueous ammonia or fused with oxide of lead, it is converted into a more soluble oxyfluoride, the solution of which has an astringent taste, and on standing in the air, deposits carbonate of lead, mixed or combined with fluoride of lead.

A chlorofluoride of lead has been already described (p. 539).

LEAD, HYDROALUMINOUS. See PLUMBORESINITE.

LEAD, IODIDE OF, PbI or $PpbI^2$, is obtained by precipitating nitrate of lead with iodide of potassium, avoiding an excess of either salt. It is a precipitate of a fine light yellow colour; soluble in 1,235 pts. of cold water (Denort), and in 194 pts. of boiling water, forming a colourless solution, whence it crystallises on cooling in flexible, six-sided, laminar crystals. It is obtained in the same form by mixing the solutions of iodide of lead and iodide of potassium at the boiling heat. It is not more soluble in water containing acetic acid than in pure water. According to Henry, it is not quite insoluble in alcohol. Ether, according to A. Vogel, extracts iodine from it, leaving oxyiodide of lead. It dissolves in cold, and still more in warm aqueous sal-ammoniac, and crystallises therefrom on cooling in yellowish white needles (Boullay). In caustic ammonia, nitrate, succinate, carbonate, and sulphate of ammonium, it turns white (Wittstein). When boiled with the carbonates of the alkalis or alkaline earths, it yields carbonate of lead and a soluble iodide.

Iodide of lead, when heated, turns reddish-yellow and brick-red, then red-brown, and melts to a liquid of the same colour, which solidifies to a yellow mass. When fused in contact with the air, it gives off a part of its iodine, and leaves an oxyiodide of lead. It is easily decomposed by chlorine. Zinc or iron boiled with it under water takes up the iodine and precipitates metallic lead.

Iodide of Lead and Hydrogen, $PbI.HI$, crystallises from a solution of iodide of lead in warm aqueous hydriodic acid, in concentrically grouped, silky needles, which give off the whole of the hydriodic acid when heated, and part of it even when exposed to the air at ordinary temperatures. The acid may also be extracted by water.

Ammonio-iodide of lead, or *iodide of plumbammonium*, NH^3PbI, is obtained as a white powder by passing ammonia-gas for a long time over finely-pulverised iodide of lead, or by digesting it at ordinary temperatures with sal-ammoniac. It gives off its ammonia spontaneously on exposure to the air, and even in an atmosphere of ammonia when heated.

Aceto-iodide of lead, $PbI.C^2H^3PbO^2$, or $\left.\begin{matrix}C^2H^3O\\ Ppb\end{matrix}\right\}\begin{matrix}O\\ I\end{matrix}$, analogous to glycolic iodacetin (ii. 568), is obtained in a similar manner to the corresponding chlorine-compound (p. 539), with which it is isomorphous. (Carius, Ann. Ch. Pharm. cxxv. 87.)

An *iodochloride of lead*, Pb^3Cl^2I, has been already described (p. 539).

An *iodide of lead and ammonium* is formed, as a white precipitate, on adding iodide of ammonium in excess to nitrate of lead.

A compound of *iodide of lead* with *chloride of ammonium*, $3NH^4Cl.2PbI$, is obtained by dropping a solution of neutral acetate of lead into a boiling mixed solution of iodide of potassium and sal-ammoniac, as long as no permanent precipitate is formed. On cooling, the double salt crystallises in slender yellow, shining needles, which, however, are decomposed by water, the sal-ammoniac dissolving out first.

Another compound, $NH^4Cl.PbI.H^2O$, crystallises in white silky needles.

Iodides of lead and potassium.—When 2 at. iodide of lead (PbI) and 1 at. iodide of potassium are dissolved in the smallest possible quantity of boiling water, the solution yields on cooling, large yellow, shining, six-sided laminæ, having the composition $KI.2PbI$ or $KI.PpbI^2$, and on dissolving these crystals in a hot solution of iodide of potassium, white silky needles, consisting of $2KI.PbI$ or $4KI.PpbI^2$, are deposited as the liquid cools. Both salts are decomposed by water and by alcohol.

LEAD ORES. The following is a list of minerals containing lead as an essential constituent, and available, when they occur in sufficient quantity, for the extraction of the metal:

Aciculite. Alkinite. Belonite. Needle-ore. Patrinite. $\left.\begin{matrix}Ppb''^2\\ Ccu'^2\end{matrix}\right\}S^3.Bi^2S^3$.

Altaïte. Telluride of lead. $PpbTe$.

Aluminate of lead (hydrated). Plumboresinite. $\left.\begin{matrix}Ppb''\\ Al'''^4\end{matrix}\right\}O^7.6H^2O$.

Anglesite. Sulphate of lead. Lead-vitriol. $\mathrm{PpbSO^4}$.

Antimonial sulphides of lead: see Boulangerite, Bournonite, Brogniardite, Freislebenite, Geocronite, Heteromorphite, Jamesonite, Kobellite, Plagionite, Zinkenite.

Antimonate of lead. Bleinierite. $\mathrm{Ppb^3Sb^2O^8.4H^2O}$.

Arseoxene. Zinkiferous vanadate of lead.

Arsenate of lead: see Mimetite.

Arsenomelane. $\mathrm{2PpbS.As^2S^3}$.

Binnite. A mixture of Arsenomelane and Scleroclase.

Bleinierite. Antimonate of lead.

Boulangerite. $\mathrm{3PpbS.Sb^2S^3}$.

Bournonite (to which is related Wölchite).

$$\mathrm{(2PpbS.Ccu^2S).Sb^2S^3} = \left.\begin{matrix}\mathrm{P\overset{\prime\prime}{p}b^2}\\ \mathrm{C\overset{\prime}{c}u^2}\\ \mathrm{S\overset{\prime\prime\prime}{b}{}^2}\end{matrix}\right\}\mathrm{S^6}.$$

Brogniardite. $\mathrm{PpbAg^2S^2.Sb^2S^3}$.

Caledonite. $\mathrm{(Ppb;Ccu)CO^3.PpbSO^4}$.

Carbonate of lead. Cerusite. White lead ore. $\mathrm{PpbCO^3}$.

Cerasin. Corneous lead. Horn-lead. Chlorocarbonate of lead. Phosgenite. $\mathrm{PpbCl^2.PpbCO^3}$.

Cerusite: see Carbonate of lead.

Chileïte. Vanadate of lead and copper. $\mathrm{6(Ppb;\ Ccu)O.VvO^3} = \left.\begin{matrix}\mathrm{(VvO^2)''}\\ \mathrm{6(Ppb;Ccu)''}\end{matrix}\right\}\mathrm{O^7}$.

Chiviatite. $\mathrm{2PpbS.3Bi^2S^3}$.

Chloride of lead. Cotunnite. $\mathrm{PpbCl^2}$.

Chlorarsenate of lead: see Mimetite.

Chlorocarbonate of lead: see Cerasin.

Chlorophosphate of lead: see Pyromorphite.

Chromate of lead: see Crocoïsite, Melanochroïte, Red lead ore, Vauquelinite.

Clausthalite. Selenide of lead. PpbSe.

Corneous lead. Syn. with Cerasin.

Cotunnite: see Chloride of lead.

Crocoïsite. Chromate of lead. $\mathrm{PpbO.CcrO^3} = \left.\begin{matrix}\mathrm{Ppb''}\\ \mathrm{Ccr^{vi}}\end{matrix}\right\}\mathrm{O^4}$.

Cupreous sulphate of lead: see Linarite.

Cupreous sulphatocarbonate of lead: see Caledonite.

Cuproplumbite. $\mathrm{2PpbS.CcuS}$.

Dechenite. Vanadate of lead. $\mathrm{PpbVvO^4}$.

Descloïzite. $\mathrm{2PpbO.VvO^3}$ or $\mathrm{PpbO.PpbVvO^4}$.

Embrothite: see Boulangerite.

Eusynchite. $\mathrm{PpbVO^3.PpbVO^4}$.

Freislebenite. $\mathrm{Ppb^3Ag^4S^5.2Sb^2S^3}$.

Galena. Lead-glance. Sulphide of lead. PpbS.

Geocronite. Arseniferous Schulzite.

Heteromorphite. Feather-ore. Plumosite. $\mathrm{2PpbS.Sb^2S^3}$.

Hydroaluminous lead: see Aluminate of lead.

Kilbrickenite. $\mathrm{6PpbS.Sb^2S^3}$.

Kobellite. $\left.\begin{matrix}\mathrm{P\overset{\prime\prime}{p}b^3}\\ \mathrm{(\frac{2}{5}S\overset{\prime\prime\prime}{b}\ \frac{3}{5}B\overset{\prime\prime\prime}{i})^2}\end{matrix}\right\}\mathrm{S^6}$.

Lanarkite. Sulphatocarbonate of lead. $\mathrm{PpbCO^3.PpbSO^4}$.

Lead-glance: see Galena.

Lead, native.

Lead ochre. Native protoxide of lead.

Lead ore, green: see Mimetite and Pyromorphite.

Lead ore, red: see Minium.

Lead ore, white: see Cerusite.

Lead ore, yellow: see Molybdate of lead.

Leadhillite. Sulphatotricarbonate of lead. $\mathrm{3PpbCO^3.PpbSO^4}$.

Lehrbachite. Selenide of lead and mercury. $\mathrm{(Ppb;Hhg)Se}$.

Linarite. Cupreous Anglesite. Cupreous sulphate of lead. $\mathrm{CcuH^2O^2.PpbSO^4}$.

Matlockite. $\mathrm{Ppb^2Cl^2O}$.

Melanochroïte. Phœnicite. Phœnocochroïte. $\mathrm{3PpbO.2CcrO^3} = \left.\begin{matrix}\mathrm{P\overset{\prime\prime}{p}b^3}\\ \mathrm{(Ccr^{vi})^2}\end{matrix}\right\}\mathrm{O^9}$.

Mendipite. $\mathrm{Ppb^3Cl^2O^2}$.

Meneghinite. $\mathrm{4PpbS.Sb^2S^3}$.

Mimetite, Mimetesite, Mimetene. Green lead ore. $\mathrm{PpbCl^2.3Ppb^3As^2O^8}$. To this is related Hedyphane, containing also calcium and phosphorus.

Minium. Red oxide of lead (p. 552).

Molybdate of lead. Wulfenite. Yellow lead ore. $\mathrm{PpbO.MmoO^3} = \left.\begin{matrix}\mathrm{Mmo^{vi}}\\ \mathrm{Ppb''}\end{matrix}\right\}\mathrm{O^4}$.

Muriocarbonate of lead. Syn. with Cerasin.

Nagyagite. Foliated Tellurium. $\mathrm{(Ppb;Au^2).(Te;Se)^2}$.

Needle ore: see Aciculite.

Oxides of lead: see Lead ochre, Minium, and Plattnerite.

Oxychloride of lead: see Matlockite and Mendipite.

Patrinite: see Aciculite.

Phœnicite or Phœnicochroïte: see Melanochroïte.

Phosgenite: see Cerasin.

Phosphate of lead: see Pyromorphite.

Plagionite. $\mathrm{4PpbS.3Sb^2S^3}$.

Plattnerite. Peroxide of lead. $\mathrm{PpbO^2}$. A doubtful species.

Plumboresinite: see Aluminate of lead.

Plumbostib: see Boulangerite.

Polysphærite. Pyromorphite containing calcium.

Polytelite. $\mathrm{4(Ppb;Ag^2)S.Sb^2S^3}$.

Pyromorphite. Green lead ore. Chlorophosphate of lead. $\mathrm{3Ppb^3P^2O^8 + PpbCl^2}$ or $\mathrm{PpbF^2}$.

Schulzite. $\mathrm{5PpbS.Sb^2S^3}$.

Selenate of lead. $\mathrm{PpbSeO^4}$.

Selenide of lead: see Clausthalite and Lehrbachite.

Stolzite: Tungstate of lead. $\mathrm{P\overset{\prime\prime}{p}bW\overset{vi}{w}O^4}$.

Sulphate of lead: see Anglesite.

Sulphatocarbonate of lead: see Lanarkite.

Sulphatotricarbonate of lead: see Leadhillite, and Sulzannite.

Sulphide of lead: see Galena.

Sulzannite. Rhombohedral sulphatotricarbonate of lead. $\mathrm{PpbSO^4.3PpbCO^3}$.

Telluride of lead: see Altaïte, and Nagyagite.

Tungstate of lead: see Stolzite.

Vanquelinite. $\left.\begin{matrix}3CcuO\\ 6PpbO\end{matrix}\right\}4CcrO^2$.

Vanadate of lead: see Descloïzite, and Eusynchite.

Vanadinite. $3PpbVvO^4.PpbCl^2$.

Wölchite: see Bournonite.

Wulfenite. Molybdate of lead.

White lead ore: see Cerusite.

Zinkenite. $PpbS.Sb^2S^3 = \left.\begin{matrix}\overset{''}{Ppb}\\ \overset{'''}{Sb}{}^2\end{matrix}\right\}S^4$.

The ores which are actually worked for lead have been already described (pp. 480, 4 1): for the rest, see the several articles.—Respecting the working of lead ores, see pp. 481—531; methods of assaying them, p. 543.

LEAD, OXIDES OF. Lead forms five oxides, viz.:

The Suboxide . . .	Pb^4O or Ppb^2O.
The Protoxide . . .	Pb^2O or $PpbO$.
The Red oxide . . .	Pb^3O^2 or Ppb^3O^4.
The Sesquioxide . . .	Pb^4O^3 or Ppb^2O^3.
The Dioxide or Peroxide .	Pb^2O^2 or $PpbO^2$.

The protoxide is a strong base; the sesquioxide and peroxide also unite with acids. The red oxide is decomposed by most acids. All the oxides of lead are easily reduced to the metallic state by charcoal at a red heat.

Suboxide. Pb^4O or Ppb^2O.—This oxide, which was discovered by Dulong, remains when oxalate of lead is cautiously heated in a retort from which the air is excluded. According to Pelouze (Ann. Ch. Pharm. xlii. 209), the retort should be heated in an oil-bath to a temperature not exceeding 300°, the heat being continued as long as any gas is given off: the gas thus evolved is a mixture of 1 vol. carbonic oxide and 3 vol. carbonic anhydride:

$$2PpbC^2O^4 = Ppb^2O + CO + 3CO^2.$$

The whole is suffered to cool before the suboxide is removed. It forms a black powder, sometimes dull, sometimes having a velvety lustre. It contains no metallic lead, for mercury extracts nothing from it, either dry or under water; neither does it contain any protoxide, for the aqueous solution of acetate of lead does not extract any protoxide from it on boiling. But when heated to dull redness, out of contact of air, it is resolved into a greenish-yellow mixture of lead and protoxide (Boussingault, Pelouze). After this treatment, mercury extracts lead from the substance, and a boiling solution of acetate of lead or acetic acid leaves the lead in the form of a network, which, when pressed together between the fingers, forms a dense mass having the metallic lustre. The suboxide heated in the air takes fire, burns with a glimmering light, and is converted into protoxide. Dilute *sulphuric*, *nitric*, *hydrochloric*, or *acetic acid* resolves it into protoxide, which combines with the acid, and very finely-divided metallic lead. The same effect is produced by a strong solution of *normal nitrate of lead*; a dilute solution, on the contrary, takes up the whole of the suboxide and forms basic nitrate of lead. The suboxide, when moistened with *water*, rapidly absorbs oxygen from the air, and is converted into the white hydrated protoxide, the action being attended with rise of temperature. A mixture of finely-divided lead and litharge does not yield the same result.

The grey pellicle which forms upon lead exposed to the air, has also, according to Berzelius, the composition Ppb^2O.

Protoxide. *Lead-oxide.* Pb^2O or $PpbO$.—This oxide occurs native as lead-ochre. a massive mineral, sometimes with scaly crystalline structure. Specific gravity 8·0, Lustre dull. Opaque. Colour between sulphur- and orpiment-yellow. Streak lighter than the colour. It does not soil. It is said to occur at Badenweiler, in Baden, and, according to Gerolt, has been ejected from the volcanoes Popocatapetl and Iztaccituall, in Mexico. It is found also at other localities in Mexico, and at Austin's mines, Wythe county, Virginia. (Dana, ii. 109.)

Protoxide of lead is obtained pure by igniting the basic nitrate, or the carbonate or oxalate of lead, in a platinum crucible, in contact with the air, taking care that the oxide does not fuse, otherwise it will take up metal from the crucible, and if heated in a porcelain crucible, would take up silica. The pure oxide thus obtained has a lemon-yellow colour, and a specific gravity of 9·4214.

On the large scale, protoxide of lead is obtained in the forms of massicot and litharge.—1. *Massicot* is prepared by heating lead to low redness on a flat hearth, and continually removing the film of oxide as it forms, till the lead-ash at first obtained is, for the most part, converted into the yellow oxide; the latter is then freed from the still remaining metallic portions by grinding and levigation.—2. *Litharge* is obtained in the oxidation of *pig-lead* containing gold and silver—the resulting lead-oxide, which is generally contaminated with silica, ferric oxide, cupric and cuprous oxide, antimonious oxide, and other oxides, is fused by the high temperature, and solidifies in a scaly, shining mass, sometimes of a yellowish tint (*Argyritis, Silber-glätte*), sometimes rather inclining to red (*Chrysitis, Goldglätte*). The oxide of copper may be completely removed by digesting the levigated litharge with aqueous solution of carbonate of ammonia (Bischof, Schw. J. 64, 65).—The antimonious oxide is left behind on dissolving the litharge in boiling nitric acid, and may then be dissolved in hydrochloric acid (Anthon, Repert. 58, 387.)—The difference between red and yellow litharge is attributed by Leblanc (J. Pharm. [3], Sept. 8, 1845) to a mere diversity of physical structure, not of chemical composition; for either modification may be obtained at pleasure by properly regulating the temperature and the rate of cooling; the red variety, which is specifically lighter than the yellow and more crystalline substance, is formed most abundantly when the cooling is slow. (See also p. 514.)

Properties.—Protoxide of lead appears to be both dimorphous and amorphous, occurring in pale-yellow rhombic octahedrons and cubes, and regular dodecahedrons, and as a red amorphous powder. By the following processes it may be obtained in the crystalline state:—1. *By slow cooling after fusion.* Litharge, when quickly cooled, solidifies in a mass of crystalline scales; but the portion which remains on the muffle sometimes crystallises in yellow, translucent, six-sided tables (Marx); in trimetric octahedrons with a distinct plane of cleavage (Mitscherlich); in regular dodecahedrons, the angles of which are indefinite, in consequence of the curvature of the faces (Gaultier de Claubry and Beudant). White lead fused by the blowpipe-flame on a copper plate or other non-reducing support, crystallises in scales on cooling; but from the middle of it there generally shoots out a mass, half a line long, sometimes in the form of a triangular pyramid, sometimes in that of a nearly perfect rhombic dodecahedron, of a hyacinth-red tint while hot, becoming sulphur-yellow and translucent as it cools, and opaque and dull when perfectly cold. This alternate fusion and crystallisation may be repeated several times.—2. *By fusion with hydrate of potassium.* If 1 part of lead-oxide and from 4 to 6 of hydrate of potassium be fused for a short time in a silver crucible at an incipient red heat, and the mass after cooling exhausted with water, the lead-oxide remains in the form of cubes and square tables (Becquerel, Ann. Ch. Phys. [2], li. 105).—3. *By treating lead-oxide with potash or soda-ley.* From a solution of lead-oxide in soda-ley, saturated while hot, placed in a stoppered bottle, and then left to itself all through the winter, the lead-oxide crystallises in small, white, translucent rhombic dodecahedrons (Houton-Labillardière, J. Pharm. iii. 335). The crystals are trimetric octahedrons, having the same angles as those obtained by fusion (Mitscherlich). Strong boiling potash-ley saturated with lead-oxide yields, on cooling, yellow scales similar to those of litharge; if the potash-solution is less fully saturated with lead-oxide, or if it has deposited the excess of that oxide in scales, no further deposition takes place till after perfect cooling, whereupon red scales are thrown down, perfectly soluble in acetic acid, and therefore free from minium; if these scales are heated, they turn yellow on cooling. Hence it appears that litharge may have a red colour without containing minium or red oxide of copper (Mitscherlich, J. pr. Chem. xix. 451).—Boiling soda-ley of 40°—41° B., saturated with hydrate of lead, yields rose-red crystals of the protoxide on cooling. These crystals yield an orange-yellow powder, similar to that of litharge. At about 400° they turn black, increase in bulk, decrepitate with loss of 0·1 per cent. of water—and when heated to low redness, assume a sulphur-yellow colour without changing their form. While still in the red state, they dissolve, though very sparingly, in nitric acid, either concentrated or dilute (Calvert, Compt. rend. xvi. 136). If hydrated lead-oxide be boiled with a quantity of aqueous alkali not sufficient to dissolve it, the undissolved portion becomes converted into crystalline anhydrous oxide; the resulting solution, when evaporated, yields more crystals of the anhydrous oxide, distinguished from the former portion by their easy solubility in alkalis, even when dilute (Frémy, J. Pharm. [3], iii. 30).—4. *By precipitating a lead-salt with excess of alkali.* Solution of neutral acetate of lead mixed with excess of ammonia and exposed to the sun for a few days, yields olive-green, very hard crystals of anhydrous oxide (Tünnermann, Kastn. Arch. xix. 339). Behrens (J. Pharm. [3], iv. 4, 18) supersaturates the sugar-of-lead solution with a quantity of ammonia sufficient to re-dissolve the precipitate; filters to separate any carbonate of lead that may have been formed; puts the filtrate into a stoppered bottle; and exposes it to the rays of the sun. After a few hours, transparent crystals make their appearance, colourless at first, but afterwards becoming yellowish, and finally yellowish-grey. Their powder is white, but assumes a dark brown-red colour after long trituration.—4 measures of solution of lead-acetate, saturated at 30°, mixed with 100 measures of boiling water, and then with 45 measures of aqueous ammonia, deposit, in the course of half a minute, a large number of very delicate, yellowish-white rhomboïdal laminæ, having a silvery lustre and united in tufts; these laminæ must be separated by levigation from the crystalline granules of hydrated oxide, which fall down at the same time, then washed with boiling water, and dried in vacuo. When ignited, they do not give off any water—or only a trace of it, with decrepitation—neither do they lose their transparency. They may be obtained without admixture of hydrate, by boiling 100 measures of a saturated solution of triplumbic acetate with 50 measures of water, adding thereto a mixture of 50 measures of water at 80°, and 8 measures of aqueous ammonia, and heating the mixture in the water-bath. In the course of a minute, crystals of the oxide separate, free from hydrate, the formation of the latter being prevented by the high temperature (Payen, Ann. Ch. Phys. [2], lxvi. 54).—5. *By placing lead in contact with air and water.* On the bottom of a leaden vessel filled with water, there are first formed a number of white flakes of hydrated basic carbonate of lead, then shining grey crystals of anhydrous oxide, partly in scales like mica, partly in rhombic dodecahedrons with cube-faces. When heated, they become opaque and orange-coloured, but without losing weight or lustre. (Yorke, Phil. Mag. [3] v. 82.)

The specific gravity of protoxide of lead is 9·20092 (Karsten), 9·277 (Herapath), 9·363 (Playfair and Joule); after fusion 9·50 (Boullay). According to Leblanc (Ann. Ch. Pharm. lvi. 235), the specific gravity of litharge is greater after slow than after quick solidification. The cubical expansion between 0° and 100° is 0·00795. At a red heat it melts to a clear dark red liquid, which solidifies to a reddish-yellow crystalline mass.

Protoxide of lead unites readily with *acids*, forming neutral and very soluble salts, and likewise exhibits a decided chlorous or negative reaction towards strong *bases*. It dissolves readily in caustic *potash* and *soda*. *Baryta*-water and *lime-water* also dissolve it, and the lime-compound is said to crystallise in sparingly soluble needles. By boiling the protoxide with milk of lime, a liquid is obtained which may be used for producing a black dye on hair, nails, horn, and wood.

An *oxide of lead and silver*, $Ag^2Pb^4O^3$ or $Ag^2Ppb^2O^3$, is obtained by adding caustic potash to a solution of a lead-salt mixed with a silver-salt, as a yellow precipitate insoluble in excess of the alkali, and thereby easily separated from admixed lead-oxide. It is easily soluble in nitric acid; blackens on exposure to light; leaves, when ignited, a mixture of lead-oxide and metallic silver; and when quietly heated in hydrogen gas is reduced to an easily fusible alloy of the two metals. (Wöhler, Pogg. Ann. xli. 344.)

Protoxide of lead dissolves, according to Bineau, in 7,000 pts. of pure water, forming a solution which decomposes most salts of the alkali-metals. The solubility is greatly diminished by the presence of certain salts, *e.g.*, sulphates, phosphates and carbonates, and increased by that of ammonia and its salts (p. 47).

Hydrate, or *Hydrated Oxide of Lead*, is obtained on adding a solution of neutral acetate of lead to excess of ammonia, as a white amorphous precipitate containing $3PpbO.2H^2O$ (Payen), or $2PpbO.H^2O$ (Schaffner), or, according to older statements, $PpbO.H^2O$ or $PpbH^2O^2$. If the solution be heated, the anhydrous protoxide is formed at the same time. When lead is immersed in pure water, hydrate of lead is formed, and partly dissolves (v. Bonsdorff). The hydrate precipitated on treating nitrate or acetate of lead with caustic potash is always mixed, according to Winkelblech, with a certain quantity of basic salt. According to other statements, however, the acid which it contains may be completely removed by digestion with a slight excess of alkali.

The hydrate prepared by precipitation with ammonia, as above, appears under the microscope to be composed of prismatic crystals. It must be protected from the air during washing, otherwise it will absorb carbonic acid. It retains its water at 100°, but gives it up at a somewhat higher temperature, and is converted into the anhydrous protoxide, which is red while hot, yellow after cooling.

Hydrate of lead takes up *ammonia*, forming the two compounds $2NH^3.Pb^2O.H^2O$ and $2(NH^3.4Pb^2O).H^2O$. (Calvert, Compt. rend. xxii. 480.)

Red Oxide of Lead. *Red Lead. Minium.* Pb^3O^2 or $Ppb^3O^4 = 2PpbO.PpbO^2$ or $PpbO.Ppb^2O^3$.—This oxide is formed when the protoxide is kept at a low red heat for a considerable time in contact with the air; also, after previous formation of hydrated protoxide and basic carbonate of lead, when lead-shavings are strewn upon water, the vessel being loosely covered, and then set aside for some months, the formation of red lead taking place chiefly on those surfaces of the metal which are exposed to the air. In like manner, drawings made with lead turn red in the course of years. (v. Bonsdorff.)

The red oxide also occurs native in certain localities, mixed with other ores of lead, and probably resulting from their oxidation, viz., at Bleialf and Kall in the Eifel, at Badenweiler in Baden; at Brillon in Westphalia; on Grassington Moor, and in Weirdale, Yorkshire; in the Isle of Anglesey, and at Austin's Mine, Wythe County, Virginia, where it accompanies cerusite.

Red lead is extensively used as a pigment, and in the manufacture of flint-glass. It is prepared on the large scale in this country, chiefly in Derbyshire, by oxidising lead in a reverberatory furnace having two *fire-hearths*, covered by an elliptically arched roof; they are situated at the extreme end of the furnace, and are separated from the middle hearth, or *lead-hearth*, by low walls or fire-bridges. The fuel used is coke. About 1,500lbs. of lead (one-tenth consisting of hard lead) are placed upon the lead-hearth, and worked about, as soon as it is melted, with an iron crutch, the oxide (massicot) as it forms being pushed to the side of the hearth. The temperature must not be raised above low redness, so that the oxide may not melt. After 24 hours, the massicot is taken out, reduced, to very fine powder by grinding and levigation, again placed upon the lead-hearth, and exposed to the same temperature as before for 48 hours, or till a sample taken out appears dark red when hot, and bright red on cooling. The furnace must then be closed, and left to cool slowly, a condition mainly essential to the success of the operation. In Germany the conversion of the massicot into red lead is effected in a peculiar furnace, in which the massicot is placed, not on a hearth, but in barrel-shaped vessels open at both ends. Sometimes the operation is repeated in order to improve the colour. Carbonate of lead may also be used, instead of massicot, for conversion into red lead, but when the temperature is properly regulated, another pigment is obtained, called *Orange Lead*. Red lead thus prepared, which, however, retains a little carbonic acid, is known as a pigment by the name of Paris red.

To free commercial red lead from the yellow oxide mixed with it, Dumas digests it repeatedly with solution of lead-acetate; Berzelius and Dalton recommend treatment with cold, very dilute acetic acid; Phillips recommends 144 pts. at most, of strong acetic acid diluted with a large quantity of water to 100 of minium, inasmuch as if more acid be used, the brown peroxide is likewise formed. According to Dumas, however, peroxide of lead is always formed in the purification of minium, before the whole of the free protoxide is extracted, even when the dilutest acetic acid is employed.

Commercial red lead likewise contains all the foreign metallic oxides—such as the oxides of copper, iron, and silver—with which the massicot or litharge used in preparing it is contaminated. Red lead is likewise often adulterated with oxide of iron, red bole or brick-dust; these substances remain undissolved when the red lead is digested in warm dilute nitric acid; boiling hydrochloric acid extracts sesquioxide of iron from the residue. When red lead thus adulterated is ignited, there remains a mixture of yellow lead-oxide and the red substances that have been added to it.

On the small scale, red lead may be obtained of very fine colour by the following processes:—1. When 4 pts. of lead-oxide, prepared by igniting white lead, are heated in a silver or platinum crucible with 1 pt. of chlorate of potassium and 8 pts. of nitre (the latter acting as a flux and thereby saving the chlorate), brown peroxide of lead is first obtained; but this, when further heated to dull redness, is converted, with intumescence and thickening of the mass, into red lead. As soon as the red lead begins to decompose at the edge of the crucible, the mass is suffered to cool, and the red lead well boiled with water containing potash.—2. By boiling peroxide of lead with aqueous plumbate of potassium, or 1 pt. of the peroxide with 5 pts. of lead-nitrate and a quantity of aqueous potash or soda sufficient to redissolve the hydrate of lead first precipitated, till a brown-red mixture of minium with a small quantity of the peroxide is produced, and digesting this mixture, after washing, with oxalic acid, which decomposes the peroxide without acting on the minium. The minium obtained by this process is rather dark-coloured, but becomes brighter when rubbed up with water; it has the same composition as that which is obtained by the ordinary method. (Levol, Ann. Ch. Phys. [3] lxxv. 108.)

Properties.—Red oxide of lead is a scarlet, crystalline-granular powder; when heated, it first assumes a finer red colour, and then turns violet. Specific gravity 8·62 (Karsten), 8·94 (Muschenbroek), 9·082 (Herapath); of native minium 4·6 [?], 8·6. (Dana, ii. 126.)

Red lead was formerly supposed, according to analyses by Richter, Wiegleb, Thomson, and Berzelius, to be a sesquioxide, Ppb^2O^3; but it is probable that the products examined by these chemists contained protoxide or carbonate of lead; for Dumas has shown that the perfectly pure red oxide specially prepared for analysis, or the commercial product freed from protoxide by digestion with solution of acetate of lead, contains 90·63 per cent. lead and 9·37 oxygen, numbers agreeing exactly with the formula Ppb^3O^4. It may be regarded either as a compound of the protoxide and peroxide of lead, $2PpbO.PpbO^2$, or perhaps of the protoxide and sesquioxide, $PpbO.Ppb^2O^3$, analogous to magnetic oxide of iron. Jacquelain (J. pr. Chem. liii. 151) found that a mixture of 1 at. $PpbO$ and 1 at. $PpbO^2$, heated to 450°, assumed a fine red colour, gave off no oxygen, and was afterwards perfectly soluble in potash-ley and glacial acetic acid. It is possible, however, that there may be more than one red oxide of lead intermediate in composition between the proto- and peroxides; for a crystallised red lead from a minium-furnace, analysed by Houton-Labillardière, exhibited the composition $3PpbO.PpbO^2$.

Decompositions.—1. By rather strong ignition, red lead is resolved into the protoxide and 2·4 per cent. of oxygen gas (Dumas).—2. By many oxidable bodies, at various temperatures, it is reduced to the protoxide. Aqueous *sulphurous* and *nitrous* acids, at ordinary temperatures, convert it respectively into sulphate and nitrate of lead; *sulphurous acid* acts very slowly in the cold, but rapidly on the application of heat. *Dichloride of tin* converts it, with a rise of temperature of 13°, into chloride of lead and stannic oxide (A. Vogel, Kastn. Arch. xxiii. 84). It is likewise reduced by boiling with a solution of *sugar*, and oxidises many organic acids. When 2 pts. of red lead and 1 pt. crystallised tartaric acid are rubbed up to a thin paste with a small quantity of water, the mixture becomes hot and whitish, and the odour of formic acid is given off (Böttger).—3. By a small quantity of *hydrochloric acid*, red lead is converted into chloride of lead, peroxide of lead, and water:

$$Ppb^3O^4 + 4HCl = 2PpbCl^2 + PpbO^2 + 2H^2O.$$

By a larger quantity of hydrochloric acid, into chloride of lead, chlorine gas, and water:

$$Ppb^3O^4 + 8HCl = 3PpbCl^2 + Cl^2 + 4H^2O.$$

—4. By *chlorine-water*, into chloride and peroxide of lead:

$$Ppb^3O^4 + Cl^2 = PpbCl^2 + 2PpbO^2.$$

Similarly with *bromine-water* (Löwig). Minium is not decomposed by mercurous nitrate or oxalic acid. (Levol.)

Heated with *strong sulphuric acid*, it yields sulphate of lead and free oxygen. By *nitric acid*, *dilute sulphuric acid*, and likewise by weaker acids, such as ordinary *acetic acid*, it is resolved into protoxide and peroxide, the former dissolving in the form of an ordinary lead-salt, while the latter remains undissolved. In *glacial acetic acid*, however, it dissolves completely; and when considerable quantities of it, but not quite sufficient for saturation, are dissolved in that acid at 40°, the liquid on cooling deposits prismatic crystals of acetate of peroxide of lead, while an acetate of the sesquioxide remains in solution (Jacquelain, J. pr. Chem. liii. 151). According to Schönbein (*ibid.* lxxxiv. 315), concentrated acetic acid shaken up for about 15 minutes with levigated minium, takes up about 9 per cent. of it, forming a solution which is quickly decomposed by heat or by dilution, but appears to be stable at $-18°$. Sulphuric acid added to this solution throws down all the protoxide of lead contained in it, leaving a pure solution of acetate of peroxide, which deposits the peroxide slowly at ordinary temperatures, quickly when warmed. Potash added to the solution of minium in acetic acid, throws down, not minium, but a mixture of the proto- and peroxides, which blues tincture of guaiacum and iodised starch-paste, reactions not produced by pure minium. The solution of minium, and that of the pure peroxide in acetic acid, immediately decolorise solution of indigo; when shaken up with finely divided zinc, iron, lead, copper, or even silver, they form acetates of these metals and lose their oxidising properties. The same solutions convert iodine into iodic acid, sulphurous acid into sulphuric acid, sulphide of lead into sulphate, and act strongly at common temperatures on oil of turpentine. (Schönbein.)

Minium likewise dissolves in cold concentrated aqueous *phosphoric* and *arsenic acids*, forming salts of the peroxide. (Jacquelain, see p. 555.)

Sesquioxide of Lead. Pb^4O^3 or Ppb^2O^3.—Hypochlorite of sodium throws down from lead-salts, a reddish-yellow mixture of sesquioxide and chloride of lead, which, if warmed or left to stand for some time, turns brown from formation of peroxide. To obtain the sesquioxide free from chloride, nitrate of lead is supersaturated with potash in sufficient quantity to redissolve the precipitate, and then treated with hypochlorite of sodium. The yellow precipitate, when washed and dried, yields a soft, non-crystalline, reddish-yellow powder, which may be dried over oil of vitriol. At a red heat, the sesquioxide is resolved into 6·47 per cent. of oxygen gas, and 96·53 per cent. of protoxide. By oxalic acid and by formic acid it is reduced to protoxide, with evolution of heat. With nitric, sulphuric, hydrofluosilicic and acetic acids, generally without the application of heat, it is converted into peroxide and a salt of the protoxide. It dissolves in cold hydrochloric acid, forming a yellow liquid from which it is again precipitated by alkalis: the liquid, however, resolves itself in a few minutes into chloride of lead and free chlorine. (Winkelblech, Ann. Ch. Pharm. li. 175.)

The sesquioxide may also be obtained by precipitating a solution of the red oxide in acetic acid (*vid. sup.*) with caustic alkalis or alkaline carbonates. If the fixed alkalis are used, the sesquioxide always retains a portion of the precipitant, which cannot be removed by washing; but by pouring the acetic solution into very dilute ammonia, separating the precipitate quickly from the liquid, washing it with hot water containing a very small quantity of acetic acid, and drying at 100°, the sesquioxide is obtained pure, having the colour of ferric oxide, and differing in external appearance from that obtained by Winkelblech, but agreeing with it in composition and reactions. When heated to 150°, it becomes darker, like ignited ferric oxide, but does not decompose.

The acetic solution of the sesquioxide may be mixed without decomposition, with from 4 to 6 times its volume of alcohol of 96° Tr. (Jacquelain, *loc. cit.*)

Dioxide or Peroxide of Lead. *Brown or puce Lead.* Pb^2O^2 or $PpbO^2$.—This oxide is obtained: 1. By exposing the protoxide suspended in water to a stream of chlorine gas. Wöhler precipitates a solution of 4 pts. of acetate of lead with a solution of 3 pts. or rather more of crystallised carbonate of sodium, and passes chlorine gas through the resulting thin pulpy mass, till the whole of the carbonate of lead is converted into brown peroxide, amounting to 2½ pts., which may then be washed. No chloride of lead is formed in this reaction, the whole of the chlorine combining with the sodium, while acetic and carbonic acid are set free.—2. By fusing protoxide of lead with chlorate of potassium at a temperature short of redness.—3. By digesting the red oxide in dilute nitric acid, which dissolves the protoxide, decanting off the nitrate of lead, and washing the remaining powder with boiling water.—4. By fusing the protoxide for a considerable time with hydrate of potassium, it then crystallises in black six-sided tables (Becquerel).—5. According to Schönbein (J. pr. Chem. lxxv. 88), it is obtained, but always mixed with protoxide, when basic acetate of lead is shaken up with aqueous peroxide of hydrogen or ozonised oil of turpentine; if, however, the oil of turpentine is in excess, the peroxide is reduced to protoxide with separation of oxygen.—6. When a solution of a lead-salt (nitrate or acetate) is electrolysed, metallic lead is deposited on the negative, and peroxide of lead on the positive electrode.

According to Becquerel (Ann. Ch. Phys. [3] viii. 405), a hydrated peroxide of lead may be obtained electrolytically.

The peroxide is also said to occur native, as plattnerite, at Leadhills in Scotland, in hexagonal prisms with replaced basic edges, pseudomorphous after pyromorphite. Cleavage indistinct. Lustre metallic adamantine. Colour iron-black. Streak brown. Opaque.

The artificially prepared peroxide is a brown powder, which when heated gives off oxygen, and is converted into red lead or the protoxide. According to Suckow, it is also reduced to the red oxide by exposure to bright sunshine. When touched with the moist hands, it gives off an odour of chlorine or peroxide of hydrogen. With *hydrochloric acid*, it yields chloride of lead and free chlorine; *nitrous acid* converts it into nitrate of lead. In an atmosphere of pure *sulphurous anhydride* it becomes red-hot, and is converted into sulphate of lead, and therefore serves to separate sulphurous anhydride from other gases. With *ammonia* it forms water and nitrate of lead; and when triturated with one-sixth of its weight of *sulphur*, it takes fire, and burns with a bright flame, forming sulphide of lead (Vauquelin); the addition of phosphorus or of strong sulphuric acid causes a strong detonation (Grindel). *Organic substances* are rapidly oxidised by it; when triturated with crystallised *tartaric acid*, it becomes red-hot, and eliminates carbonic anhydride and formic acid (Walker). With $\frac{1}{8}$th *grape sugar*, vivid ignition likewise takes place; also with *mannite*, or with $\frac{1}{8}$th of *cane sugar*. *Racemic acid*, and especially *gallic acid*, also take fire in contact with it; a less violent action takes place with *mucic* and *oxalic* acids, carbonic anhydride being formed in the latter case (Böttger). The peroxide likewise oxidises organic compounds in presence of water; thus it converts *uric* acid into allantoïn and urea, forming at the same time oxalate of lead and carbonic anhydride (Liebig and Wöhler). Boiled with *grape-sugar* and water, it oxidises the sugar, producing formic acid and carbonate of lead. (Stürenburg.)

According to Munck af Rosenschöld, it is the strongest of all negative electromotors (ii. 421).

Peroxide of lead does not unite readily with *acids;* compounds of this oxide with acetic, phosphoric, arsenic acid, &c., may however, be produced by treating red lead with the respective acids. (See p. 553.)

The prismatic crystals of acetate of peroxide of lead, or peroxyplumbic acetate, which separate from a solution of red lead in glacial acetic acid may be dried to a certain extent between bibulous paper, but if the paper be renewed to complete the drying, the crystals turn yellow, and are resolved into acetic acid and the brown peroxide; if still moist with acetic acid, they may be kept undecomposed in closed vessels. They melt at 160°, and at a somewhat higher temperature, decompose quickly and completely, leaving metallic lead, and emitting an odour of acetone and acetic acid. When moistened with water, they are resolved into acetic acid and peroxide of lead; the latter may be obtained pure by washing them with hot water. This reaction affords an easy means of distinguishing between the solution of the crystals of peroxyplumbic acetate in acetic acid, and that of the sesquioxide in the same acid, as the latter yields, besides free peroxide and acetic acid, a certain quantity of neutral acetate of lead, which may be detected in the water. (Jacquelain, J. pr. Chem. liii. 151.)

A solution of peroxyplumbic phosphate is obtained by dissolving minium in moderately concentrated aqueous phosphoric acid, and precipitating the dissolved protoxide with dilute sulphuric acid. The solution may be facilitated by mixing the phosphoric acid with sulphuric, nitric, or acetic acid. Peroxyplumbic phosphate is more stable than the acetate, but on boiling the solution, oxygen is rapidly evolved, and protoxide of lead remains dissolved, without separation of peroxide. The same decomposition takes place slowly at common temperatures. Phosphoric acid added to a solution of peroxyplumbic acetate increases its stability, and prevents the separation of peroxide.—A corresponding arsenate may be obtained in like manner, but it is more prone to decomposition than the phosphate.—A concentrated solution of tartaric acid shaken up with minium takes up peroxide, and a clear solution may be decanted from the residue, but the dissolved peroxide is quickly decomposed, its oxygen oxidising a portion of the tartaric acid, and a precipitate of ordinary tartrate of lead being formed.

With *bases*, peroxide of lead unites more readily than with acids, behaving towards alkalis like a weak acid, and may therefore be called plumbic acid.

Plumbate of potassium, $K^2O.Pb^2O^2.3H^2O$ or $K^2PpbO^3.3H^2O$, is obtained in small crystals by fusing the peroxide with excess of hydrate of potassium, and dissolving the product in a small quantity of water. The solution, evaporated in a vacuum, yields rhombohedral crystals (Frémy, J. Pharm. [3] iii. 32). It may also be prepared by boiling the peroxide in a silver dish with very strong potash-ley, till a sample dissolved in water yields a copious precipitate of the peroxide on addition of nitric acid. A little water is then poured upon the hot mass, and the resulting solution is decanted and left to cool; it then deposits plumbate of potassium in octahedrons (Regnault). The crystals are decomposed by a small quantity of water, yielding peroxide of lead, and a solution of that oxide in the excess of alkali, which, however, is decomposed by a larger quantity of water, the whole of the peroxide being precipitated as a brown powder.

The solution of plumbate of potassium forms with metallic salts precipitates of analogous composition.

Plumbate of calcium is obtained by digesting nitrate of lead at 57° for five hours, with excess of lime and chloride of lime. A colourless insoluble compound is then formed, from which acids withdraw the lime, leaving pure peroxide of lead. (Crum, Ann. Ch. Pharm. lv. 218.)

LEAD, OXYBROMIDE OF. Pb^4Br^2O or $Ppb^2Br^2O = PpbBr^2.PpbO$.—This compound is formed by igniting bromide of lead in contact with the air till it ceases to emit white fumes (Balard); by heating bromocarbonate of lead (p. 540), till all the carbonic anhydride is expelled (Löwig); or by immersing bromide of lead for some days in a solution of the acetate, and agitating from time to time. It is a yellow powder, which when heated to fusion, gives off dense white fumes, and solidifies on cooling to a yellowish-white, translucent, pearly mass. When decomposed at a high temperature by chlorine, it yields 94·9 per cent. chloride of lead.

LEAD, OXYCHLORIDES OF. Chloride of lead unites in five different proportions with the protoxide, forming the following compounds:

a. $Ppb^4Cl^6O = 3PpbCl^2.PpbO$.—Four parts of chloride of lead ignited with one part of litharge yield a fused laminar pearl-grey mixture, which when triturated with water swells up to a bulky mass, having the above composition. (Vauquelin.)

b. $Ppb^2Cl^2O = PpbCl^2.PpbO$.—This compound occurs native as matlockite, in the old mine of Cromford, near Matlock in Derbyshire. It forms dimetric tabular crystals exhibiting the combination, $oP\ .\ \infty P\infty\ .\ P\ .\ 2P\infty$. Angle $P : P$ in the terminal edges = 104° 6′; in the basal edges = 120° 52′. Cleavage basal, not perfect. Hardness = 2·5 to 3. Specific gravity = 7·21—5·3947. Lustre adamantine, occasionally pearly. Colour clear yellowish, sometimes a little greenish. Transparent to translucent. (Greg, Phil. Mag. [4] ii. 120; Rammelsberg, Pogg. Ann. lxxv. 141.)

The same compound is formed by igniting chloride of lead in contact with the air, till it no longer fumes, or by fusing chloride and carbonate of lead together. Carbonic anhydride is then set free, and a compound is formed which is deep yellow while fused, but on cooling assumes a lemon-yellow colour, and becomes nacreous and crystalline (Döbereiner). It is also obtained as a hydrate, $2Ppb^2Cl^2O.H^2O$, when recently precipitated chloride of lead is digested in a cold solution of neutral acetate of lead; also when a solution of common salt is dropped into the neutral acetate. The precipitate when heated gives off its water and melts to a deep yellow mass, becoming nearly white on cooling.

Pattinson prepares this oxychloride on the large scale, for use as a pigment, by the following process:—Finely pulverised galena is heated with strong hydrochloric acid, whereby chloride of lead is formed, and sulphydric acid evolved; this gas is collected in large gasometers, and used for the preparation of sulphuric acid by combustion in the ordinary lead-chambers. The liquid is allowed to cool completely in contact with the undissolved residue; this residue, which consists chiefly of chloride of lead, is washed with cold water to remove the easily soluble chlorides of copper and iron, and then gradually introduced into a vessel containing boiling water, which dissolves the chloride of lead, leaving a smaller residue consisting of gangue, chloride of silver, and undecomposed galena. By melting this last residue with lime, a quantity of silver containing a little lead is obtained, even from ores in which the proportion of silver is too small for profitable extraction, either by the ordinary process of calcination, or by Pattinson's condensation process. The hot clear solution of chloride of lead obtained as above is mixed with very thin milk of lime, sufficient to neutralise only half the hydrochloric acid present. A precipitate of oxychloride, Ppb^2Cl^2O, is then formed, which may be used advantageously as a pigment in place of white lead, as it covers well when mixed with oil, and does not turn yellow in the dark, or blacken from exposure to air containing sulphuretted hydrogen, more quickly than white lead.

c. $Ppb^3Cl^2O^2 = PpbCl^2.2PpbO$.—This compound forms the rare mineral mendipite (also called *berzelite* and *cerasite*) found on the Mendip Hills in Somersetshire, where it occurs in yellowish-white, trimetric prisms exhibiting the faces, oP, ∞P, $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, and having the angle $\infty P : \infty P = 102° 36'$. Cleavage very distinct, parallel to ∞P; less distinct diagonally. Hardness = 2·5—3. Specific gravity = 7 to 7·1. The crystals are translucent, and have an adamantine lustre on the cleavage-faces. It occurs in a state of greater purity at Brilon, near Stadtbergen in Westphalia; the crystals there found are white, translucent, and have a mother-of-pearl lustre on the cleavage-faces. It is also found in opaque prismatic crystals at Tarnowitz in Silesia.

d. $Ppb^4Cl^2O^3 = PpbCl^2.3PpbO$.—This compound is obtained in the anhydrous state by fusing 1 at. chloride of lead with 3 at. of the protoxide; also as a hydrate, $Ppb^4Cl^2O^3.H^2O$, by decomposing chloride of lead with ammonia; by precipitating basic acetate of lead with common salt; and by decomposing a solution of common salt with protoxide of lead. The hydrate is a white flocculent mass, and when ignited leaves the anhydrous compound, which is a greenish-yellow laminated mass, yielding a yellow powder, known as *Turner's yellow.* It is prepared as a pigment, by mixing litharge with ¼ to ⅛ of its weight of common salt, and pouring water on the mixture; it then becomes hot, swells up, yields a solution of caustic soda containing a very small quantity of lead, and a residue of basic chloride, which is washed and ignited at a moderate heat. The hydrated compound was formerly used as a white pigment in place of white lead, being known as *Pattinson's monobasic chloride;* but it has not so much body as white lead.

e. $Ppb^4Cl^2O^5 = PpbCl^2.5PbO$.—Obtained by fusing chloride of lead with 5 at. of the protoxide. Orange-yellow substance, yielding a deep yellow powder.

f. $Ppb^8Cl^2O^7 = PpbCl^2.7PpbO$.—Produced by fusing a mixture of 10 pts. of pure oxide of lead and 1 pt. of pure sal-ammoniac, a portion of the lead being at the same time reduced. The fused product affords cubic crystals on cooling slowly. It forms in that state a beautiful yellow pigment, known as *Cassel yellow.*

LEAD, OXYCYANIDE OF. See ii. 253.

LEAD, OXYFLUORIDE OF. See p. 547.

LEAD, OXYGEN-SALTS OF. Protoxide of lead is a strong base, uniting readily with acids, and forming salts, the general characters of which have been already described (p. 540). Those which are soluble have a sweetish taste and are poisonous. They resemble the salts of barium and strontium in being readily precipitated by sulphuric acid, and many of them are isomorphous with the corresponding salts of those metals. Lead has a very great tendency to form basic salts, which may be regarded either as compounds of the normal salts with oxide or hydrate of lead, or as salts derived from two or more molecules of water, in which less than half the hydrogen is replaced by an acid radicle: thus, there is a basic nitrate of lead containing $PbNO^3.PbHO$ or $\left.\begin{matrix}NO^2\\ \overset{\prime\prime}{Ppb}\\ H\end{matrix}\right\}O^2$, and a tribasic acetate containing $C^2H^3PbO^2.Pb^2O$ or $\left.\begin{matrix}C^2H^3O\\ Pb^3\end{matrix}\right\}O^3$ or $\left.\begin{matrix}(C^2H^3O)^2\\ \overset{\prime\prime}{Ppb}{}^3\end{matrix}\right\}O^4$. These basic oxygen-salts are analogous to the oxychlorides, oxyiodides, &c. (For descriptions of the individual salts, see the several ACIDS.)

The sesquioxide and peroxide of lead also unite with acids, but the salts thence resulting are not very stable. They are produced by the action of certain acids on the red oxide of lead (p. 553).

LEAD, OXYIODIDES OF. Five of these compounds have been described:

a. $Ppb^2I^2O = PpbI^2.PpbO$, is obtained, according to Brandes and Kühne (Pharm. Centralbl. 1847, p. 593), by precipitating acetate of lead with iodide of potassium. Denot (J.-Pharm. xx. 1) uses a solution of the neutral acetate mixed with a small quantity of basic acetate, and dissolves out the iodide of lead contained in the precipitate with water. The same compound is said to be formed when iodide of lead is digested for some time in a solution of the neutral acetate. Acetic acid is said to dissolve out the oxide of lead from this compound, leaving the iodide. By immersion in solution of iodide of potassium it is converted into iodide of lead. It contains 1 at. water, which is given off at 100° (Kühne), at 200° (Denot). It melts with partial decomposition at 300°, and solidifies to a clear yellow glass on cooling.

b. $Ppb^3I^2O.H^2O = PpbI^2.2PpbO.H^2O$, is obtained, according to Kühne, by digesting levigated oxide of lead with a boiling solution of iodide of potassium as long as it continues to increase in weight. By precipitating basic acetate of lead with iodide of potassium, Kühne obtained nothing but the compound *a*, whereas Denot states that compounds containing 2 at. and 5 at. oxide of lead to 1 at. iodide are obtained by precipitating iodide of potassium with dibasic or pentabasic acetate of lead.

c. $PpbI^2.3PpbO.2H^2O$.—Obtained by treating a boiling solution of iodide of lead with caustic ammonia. (Kühne.)

d. $PpbI^2.2PpbO.Ppb^2O^3$ (?).—This is a wine-red compound, obtained by triturating recently precipitated hydrate of lead with a fourth of its weight of iodine, and boiling with water as long as fumes of iodine are given off. (Jammes.)

e. $PpbI^2.5PpbO$.—Remains in the form of a yellow powder when the compound *d* is dried and heated. (Handw. d. Chem. 2te Aufl. ii. [2], 60.)

LEAD, PHOSPHIDE OF. *a.* When phosphorus is thrown upon melted lead, or when lead-filings are ignited with an equal weight of glacial phosphoric acid, or chloride of lead with phosphorus, a compound is formed containing not more than 15 per cent. of phosphorus: it has the colour of lead; may be cut with a knife, but splits into laminæ when hammered; tarnishes quickly when exposed to the air; and, when heated before the blowpipe, yields a phosphorus-flame and a globule of lead (Pelletier, Ann. Ch. Phys. [2], xiii. 114).—*b.* Phosphoretted hydrogen gas passed for two hours through a solution of neutral acetate of lead, yields a brown precipitate, which burns before the blowpipe with a small phosphorus-flame, forming beautifully crystallised lead-phosphate. (H. Rose, Pogg. Ann. xxiv. 326.)

LEAD, SELENIDE OF. Very small quantities of selenium combined with lead render it harder and less fusible.

The *protoselenide*, Pb^2Se or $PpbSe$, is formed when lead and selenium are heated together, combination then taking place attended with incandescence, and a grey porous mass being formed, which becomes silver-white by polishing. When ignited in an open vessel, it first gives off selenium, then a small quantity of selenide of lead in white fumes, leaving a residue of basic selenite of lead. Cold nitric acid dissolves the lead, leaving red selenium, which, on heating the liquid, dissolves in the form of selenious acid. (Berzelius.)

Selenide of lead also occurs native, as clausthalite, sometimes pure, sometimes having part of the lead replaced by other metals, as cobalt, copper, mercury, and silver. It is found in fine-grained masses, sometimes foliated, with cubic cleavage. Hardness = 2·5 to 3. Specific gravity = 7 to 8·8. Lustre metallic. Colour lead-grey, sometimes bluish; cupreous varieties yellowish. Streak darker. Opaque. Fracture granular and shining. Rather sectile. Before the blowpipe it emits the odour of horseradish and exhibits various other reactions characteristic of selenium (*q. v.*). Heated in a tube it yields a sublimate of selenium.

The following are analyses of clausthalite and its varieties:—*a*, H. Rose (Pogg. Ann. ii. 416; iii. 281); *b*, Stromeyer (*ibid.* ii. 403); *c*, Selenide of lead and silver (Rammelsberg, *Mineralchemie*, p. 34); *d*, Selenide of lead and cobalt; *e*, *f*, Selenides of lead and copper (H. Rose, Pogg. Ann. iii. 288); *g*, *h*, The same (Kersten, *ibid.* xlvi. 265):

	Tilkerode.	Clausthal.	Tilkerode.	Clausthal.	Tilkerode.		Glasbach.	
	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Selenium . .	27·59	28·11	26·52	31·42	34·98	30·26	32·09	29·97
Lead . . .	71·81	70·98	60·15	63·92	48·43	60·28	57·48	65·16
Silver . . .	. .	. .	11·67	. .	1·32			
Cobalt. . .	. .	0·83	. .	3·14	. .	. .	0·05	0·08
Copper . .	. .	. .	. .	. .	15·77	7·94	8·58	4·09
Iron . . .	. .	. .	. .	0·45	. .	0·78		
	99·40	99·92	98·34	98·93	100·50	99·26	98·20	99·30

The varieties *e*, *f*, *g*, *h*, which contain copper, are by some mineralogists regarded as distinct species; but it is perhaps better to regard them as varieties of clausthalite, in which part of the lead is replaced by copper; *e* and *f* are called *raphanosmite* by Kobell; *d* is called *Tilkerodite* by Haidinger; *d*, *e*, and *f* are called *Zorgite* by Brooke and Miller; *e* and *h* agree nearly with the formula $\left.\begin{matrix}\frac{3}{4}\mathrm{Ppb}\\\frac{1}{4}\mathrm{Ccu}\end{matrix}\right\}\mathrm{Se}$; *f* and *g* with $\left.\begin{matrix}\frac{7}{8}\mathrm{Ppb}\\\frac{1}{8}\mathrm{Ccu}\end{matrix}\right\}\mathrm{Se}$.

Clausthalite and its varieties occur at Harzgerode, in the Hartz, and at Clausthal, Tilkerode, Zorge, Glasbach, near Hildburghausen, and Lehrbach; also at Ramsberg and Freiberg in Saxony.

Lehrbachite, which is a selenide of lead and mercury, and is described as having the structure and colour of clausthalite, is, perhaps, a mechanical mixture of that mineral with selenide of mercury. It emits the odour of selenium before the blowpipe, and gives mercury with soda. H. Rose found in one specimen 24·97 per cent. selenium, 55·84 lead, and 16·94 mercury (= 97·75); in another, 27·98 selenium, 27·33 lead, and 44·69 mercury (= 100).

LEAD, SULPHIDES OF. There are four compounds of lead and sulphur, namely, the protosulphide, two subsulphides, and a persulphide; but the protosulphide is the only one whose constitution is accurately known.

Tetartosulphide. Pb^8S or Ppb^4S?—A finely divided mixture of 100 pts. of galena and 84 of lead heated for a quarter of an hour in a well-closed charcoal-lined crucible, placed in a wind-furnace with a strong draught, yields 144 pts. of a dull, lead-coloured, fine-grained, semi-malleable, soft mixture, exhibiting a dark-grey colour on the cut surface. When oxidised by nitric acid, it yields 36 per cent. of lead-sulphate, and must therefore contain 3·96 per cent. of sulphur. (Bredberg, Pogg. Ann. xvii. 274.)

Hemisulphide. Pb^4S or Ppb^2S.—1. By the same process as for the preceding compound—excepting that the mixture is fused in an earthen instead of a charcoal-lined crucible, and covered with borax—150 pts. of a more brittle mixture are obtained, having a dark leaden-grey colour, a finely laminar fracture, and containing 7·207 per cent. of sulphur (Bredberg).—2. Sulphate of lead ignited in a charcoal-lined crucible gives off sulphurous anhydride and leaves hemisulphide of lead, which at a higher temperature, partly volatilises and is partly decomposed, leaving a residue of metallic lead. (Berthier, Ann. Ch. Phys. [2] xxii. 240.)

Protosulphide. Pb^2S or PpbS.—This compound is found native as galena (*blue lead*, *galène*, *Bleiglanz*), the most abundant and important ore of lead. It occurs frequently in very fine crystals belonging to the monometric system, with cubic cleavage, perfect and easily obtained. The ordinary forms are the octahedron, cube, and rhombic dodecahedron, occurring alone or in combination with other forms, 2O for example, subordinate; twins like *fig.* 320 (ii. 160), and others in which the intersecting cubes are of different sizes, or in which the diagonals do not exactly coincide; also pseudomorphs after pyromorphite. The crystals are frequently imbedded, or united in granular aggregations. The mineral likewise occurs in tabular, reniform or botryoïdal masses, coarse or fine granular, sometimes impalpable, occasionally fibrous. Hardness = 2·5. Specific gravity = 7·25 to 7·7. Lustre metallic. Colour and streak pure lead-grey; surface of crystals occasionally tarnished. Fracture scarcely perceptible in the crystals, on account of the perfect cleavage; in the massive varieties, flat sub-conchoïdal, or uneven. Before the blowpipe, it decrepitates strongly, melts and yields a globule of lead as soon as the sulphur is volatilised.

For analyses of galena, see p. 480.

Galena is found abundantly in England and in many parts of Europe; in the Daouria Mountains, Siberia; in Algeria; near the Cape of Good Hope; in Australia; and in many parts of North America. It occurs in beds and veins, both in crystalline and uncrystalline rocks, often associated with blende, iron and copper pyrites, carbonate of lead and other lead ores, and in a gangue of heavy spar, calcspar or quartz. It often suffers decomposition, and gives rise to the formation of other plumbiferous minerals.

Breithaupt's antimonial galena from Freiburg in the Breisgrau, with specific gravity = 6·9 to 7·0, is perhaps the same as steinmannite from Przibram in Bohemia. Whether the tetragonal galena of the same mineralogist, also containing antimony, is a dimetric variety of galena, is not exactly known.

Protosulphide of lead is produced artificially:—1. When sulphur is mixed with melted lead, the whole becoming red-hot. Strips of lead even of moderate thickness, take fire in sulphur-vapour, and burn with vivid glow, depositing half-fused globules of the protosulphide.—2. By heating the protoxide with excess of sulphur.—3. By the action of sulphydric acid or an alkaline sulphide on the oxide or salts of lead.—4. Becquerel, by immersing cinnabar in a solution of chloride of magnesium contained in a glass tube, dipping a lead plate to the bottom, and leaving the tube well closed for six weeks, obtained grey, metallic-shining, regular tetahedrons of the protosulphide, which formed on the sides of the tube.

Sulphide of lead obtained by fusing its elements together is of a lead-grey colour, with granular fracture; that which is precipitated by sulphydric acid is a brown-black powder, and, according to Karsten, has a density of 7·5052 after fusion. Sulphide of lead melts at a strong red heat, volatilises at a stronger heat, and sublimes undecomposed if kept from contact with the air.

Decomposition.—1. Sulphide of lead, when gently ignited in the air, gives off the greater part of its sulphur in the form of sulphurous anhydride, while metallic lead (amounting to about half the total quantity) and sulphate of lead remain behind (Descotils, Ann. Ch. Phys. [2] lv. 441).—2. The protosulphide and protoxide of lead decompose one another when heated together, evolving sulphurous anhydride and leaving metallic lead:

$$PpbS + 2PpbO = Ppb^3 + SO^2.$$

—3. The protosulphide heated in vapour of water gives off sulphydric acid and yields metallic lead. The first products formed are sulphydric acid and the protoxide, which then reacts on the remaining sulphide in the manner just described.—4. When sulphide of lead is fused with alkaline carbonates, half the lead is separated in the metallic state, and on addition of metallic iron, the whole.

Protosulphide of lead is insoluble in *dilute acids*, in caustic *alkalis*, and *alkaline sulphides*. When boiled with *dilute nitric acid* it gradually dissolves as nitrate, with evolution of nitric oxide, and separation of sulphur. The finely divided sulphide treated with *fuming nitric acid* is completely converted into sulphate of lead; but if any portion of the sulphur remains unoxidised, a corresponding quantity of the lead is converted into nitrate. By strong *hydrochloric acid* it is converted into chloride of lead with evolution of sulphydric acid. *Nitro-hydrochloric acid* converts it into chloride and sulphate of lead. *Chlorine* decomposes it slowly, forming chloride of lead and chloride of sulphur.

Persulphide. A solution of a lead-salt mixed with pentasulphide of potassium yields a precipitate, which has at first a fine blood-red colour, but quickly loses this colour, even while immersed in the liquid, and is resolved into the protosulphide and free sulphur. Higher sulphides of lead are also said to be formed by the action of sulphydric acid on the sesquioxide and peroxide of lead; but their composition has not been made out.

LEAD, SULPHOCARBONATE OF. See SULPHOCARBONATES.

LEAD, SULPHOCHLORIDE OF. If a lead-salt, *e.g.* aqueous chloride of lead, be precipitated by a mixture of aqueous sulphydric and hydrochloric acids, there is produced, first a yellowish-red, and then a red precipitate containing about 56 per cent. (3 at.) of lead-sulphide, and agreeing very nearly with the formula, $PpbCl^2.3PpbS$. An excess of sulphydric acid turns it black and converts it into pure sulphide of lead; the same change is produced by boiling with water, which extracts the chloride; the compound is also blackened by potash, which extracts the chlorine (Hünefeld, J. pr. Chem. vii. 27).—When sulphydric acid gas is passed through a solution of ½ pt. lead-acetate in 100 pts. of water mixed with 10 pts. of hydrochloric acid of specific gravity 1·168, a beautiful carmine-coloured precipitate of sulphochloride of lead is produced. If the solution contains 1 pt. of lead-acetate, 112 pts. of water, and 14 of strong hydrochloric acid, sulphydric acid produces a yellow precipitate, which gives up chloride of lead to boiling water, while black protosulphide of lead remains behind.—If, instead of 14 pts. of strong hydrochloric acid, we use 14 pts. of a mixture of 2 pts. of strong hydrochloric and 1 pt. nitric acid, prepared two days before and containing pernitric oxide, the sulphydric acid produces, after a while, first a yellowish-red and then a cinnabar-red, granular precipitate. If the stream of sulphydric acid gas were continued for a longer time, the precipitate would become first carmine-coloured, then brown, and lastly black. The red granular precipitate, when boiled with water, gives up a considerable quantity of chloride of lead, and is converted into a brown-red, flocculent powder, which then undergoes no further change, but when heated alone in a glass tube, gives off sulphur and sulphydric acid, and fuses to a brown mass. According to this reaction, the pernitric oxide must have precipitated sulphur from the sulphydric acid, and the red precipitate is a compound of the chloride with a polysulphide of lead. (Reinsch, J. pr. Chem. xiii. 130.)

LEAD, SULPHOCYANATE OF. See SULPHOCYANATES.

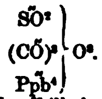
LEAD, WHITE. Hydrated carbonate of lead used as a pigment (ii. 786). The native anhydrous carbonate is also called white lead ore.

LEAD-GLANCE. Syn. with galena (see p. 558).

LEAD-GLASS. *Vitrum plumbi.*—A term formerly applied to perfectly fused oxide of lead. Oxide of lead is used as an ingredient in various kinds of glass, as in flint-glass, crystal-glass, strass, &c. (ii. 841).

LEAD-GLAZE. The glaze of the more common kinds of earthenware consists of an easily fusible silicate of lead, prepared from a mixture of finely ground red lead, litharge, white lead, or galena, with clay or sand. It melts more easily in proportion as it is richer in lead, but when the proportion of lead is very large, the glaze is decomposed by dilute acids, which dissolve part of the oxide of lead.

LEADHILLITE. *Sulphato-tricarbonate of lead,* $Pb^2SO^4.3Pb^2CO^3$ =



$$\left.\begin{matrix}\overset{\prime\prime}{S}O^2\\ (\overset{\prime\prime}{C}O)^3\\ P\overset{\prime\prime}{p}b^4\end{matrix}\right\}O^8.$$

—A crystallised mineral occurring, together with other ores of lead, at Leadhills in Scotland; said also to be found in Grenada, in the island of Serpho, Grecian Archipelago, and in the Newberg district, South Carolina. The crystals are trimetric, exhibiting the planes $\infty\breve{P}\infty$ (greatly predominant), $\infty\bar{P}\infty$, ∞P, $\frac{2}{3}\bar{P}\infty$, $\frac{2}{3}P$; $\frac{1}{3}\breve{P}\infty$; $\frac{1}{3}P$ and others. Angle $\infty P : \infty P = 103° 16'$. Ratio of principal axis, brachydiagonal and macrodiagonal = 1·7205 : 1 : 1·2632. The crystals are hemihedral in ∞P and some other planes; hence they are monoclinic in aspect, or rhombohedral when in compound crystals. Cleavage very perfect parallel, to $\infty\breve{P}\infty$; in traces parallel to $\infty\bar{P}\infty$. Twins consisting of three crystals, with face of composition $\breve{P}\infty$; also parallel to ∞P. Hardness = 2·5. Specific gravity = 6·2—6·5. Lustre of $\infty\breve{P}\infty$ pearly, of the other faces resinous, somewhat adamantine. Colour white, passing into yellow, green, and grey. Streak uncoloured. Transparent to translucent. Conchoïdal fracture scarcely observable. Rather sectile. Before the blowpipe, it intumesces at first, then turns yellow, but becomes white on cooling; easily reduced on charcoal. It effervesces briskly in nitric acid, and leaves a white residue of lead-sulphate.

Berzelius found in the mineral 28·7 per cent. sulphate, and 71·0 carbonate of lead (= 99·7); Stromeyer found 28·3 sulphate, and 72·7 carbonate (= 100); the formula requires 27·44 sulphate and 72·56 carbonate. (Dana, ii. 371.)

LEAD-MATT. *Matte de plombe. Bleistein.*—This term is applied to the mixtures of sulphide of lead with other metallic sulphides, chiefly sulphide of iron, obtained in the metallurgic treatment of lead-ores (p. 492).

LEAD-OCHRE. Native protoxide of lead (p. 550).

LEAD-PLASTER. A mixture of the lead-soaps of fatty acids, used in medicine as an external application. It is prepared by heating 9 pts. of olive-oil (sometimes also lard or rape-oil) nearly to its boiling-point, then adding by degrees 5 pts. of powdered litharge, incorporating thoroughly with a spatula, adding from time to time small portions of warm water, and continuing the heating and incorporation till a few drops of the mixture harden when thrown into water, and form a glutinous mass between the fingers. Sometimes a mixture of litharge and white lead is used instead of litharge alone.—Well-prepared lead-plaster forms a whitish-yellow homogeneous mass, somewhat flexible and tenacious in summer, brittle in winter. When gently heated, it melts to a thick liquid, which, at higher temperatures, turns brown, and finally black, giving off irritating vapours.

LEAD-RADICLES, ORGANIC. These compounds, the series of which is at present far from complete, are obtained by the action of the iodides of the alcohol-radicles on lead or its alloys with potassium or sodium, or of zinc-ethyl on chloride of lead. The formation of ethyl-compounds by the first of these processes was first observed in 1853 by Löwig (J. pr. Chem. lx. 304; Ann. Ch. Pharm. lxxxviii. 318), soon afterwards by Cahours and Riche. (Compt. rend. xxxvi. 1002.)

The iodide of the radicle $Pb^2(C^2H^5)^3$, or $Ppb(C^2H^5)^3$, was separated by Löwig, who designated the radicle methplumbethyl, and studied several of its compounds, but did not obtain it in the free state. It has since been isolated (1860) by Klippel (J. pr. Chem. lxxxi. 287), who has likewise obtained the corresponding amyl-compound.—The compound $Pb(C^2H^5)^2$ or $Ppb(C^2H^5)^4$ was discovered in 1858 by Buckton (Phil. Mag. [4] xviii. 212, xvii. 282; Ann. Ch. Pharm. cix. 218, cxii. 220); and the corresponding methyl-compound by Cahours in 1861 (Ann. Ch. Phys. [3] lxii. 257; Ann. Ch. Pharm. cxxii. 48), who likewise obtained by its decomposition, the compound $Pb^2(CH^3)^3$ or $Ppb(CH^3)^3$.

Amyl-compounds.

Plumbotriamyl. *Methplumbamyl.* $Pb^2C^{15}H^{33} = Ppb(C^5H^{11})^3 = PpbAm^3$.—Prepared (like the corresponding ethyl-compound) by distilling an alloy of lead and sodium with iodide of amyl, shaking up the distillate with ether, distilling off the ether after addition of a little alcohol, and treating the residue with a large quantity of water. Plumbotriamyl then separates as a yellowish, oily, non-volatile liquid, inodorous in the cold, smelling like plumbotriethyl when warm: its vapour exerts an irritating action on the mucous membranes. When set on fire it burns, with separation of lead-oxide. With fuming nitric acid it detonates, with emission of light and heat.

The *chloride*, $PpbAm^3Cl$, is obtained by treating the oxide (*infra*) with hydrochloric acid. It crystallises in white needles.

The *iodide*, $PpbAm^3I$, is obtained in white needles by adding iodine to the ethereal solution of plumbotriamyl, till the colour becomes permanent, and evaporating the filtrate. It is more stable than the corresponding ethyl-compound, melting at 100° without decomposition, and solidifying in the crystalline form on·cooling. It is insoluble in water. It unites with *mercuric iodide*, forming the double salt $PpbAm^3I.HhgI^2$, which crystallises in golden-yellow laminæ, insoluble in water, sparingly soluble in alcohol and ether.

Oxide.—By agitating the alcoholic solution of the iodide with recently precipitated oxide of silver, evaporating the filtrate, and treating the residue with water, oxide of plumbotriamyl separates as a faintly yellow viscid mass, insoluble in water, soluble in alcohol and ether; the alcoholic solution has a faint alkaline reaction, and precipitates ferric salts, but not copper or silver salts.

The *sulphate*, obtained by heating the oxide with dilute sulphuric acid, is a viscid uncrystallisable mass. (Klippel.)

Ethyl-compounds.

Plumbotriethyl. $Pb^2C^6H^{15} = Ppb(C^2H^5)^3 = PpbE^3$. Löwig's *Methplumbethyl.*—Löwig, by acting on an alloy of 6 pts. lead and 1 pt. sodium with iodide of ethyl, obtained a mixture of several lead-compounds of ethyl, which he was not able to separate. The mixture was perfectly colourless, tolerably mobile, volatile, and had a powerful odour; did not fume in the air, but when set on fire burnt and gave off dense clouds of oxide of lead. It took fire when strong nitric acid was poured upon it, and exploded with great violence in contact with iodine or bromine. It was insoluble in water, but dissolved readily in alcohol or ether; and the solutions, when exposed to the air, deposited an amorphous powder, insoluble in water, alcohol and ether, but capable of forming crystallisable salts with acids, while in solution there remained a strongly alkaline base, the oxide of plumbotriethyl, the radicle of which appeared to constitute the greater part of the product. This radicle, however, Löwig did not succeed in isolating.

Klippel prepares an alloy of lead and sodium, having nearly the composition $PpbNa^3$, by melting 3 pts. of lead in a hessian crucible, and after removing it from the fire, adding 1 pt. sodium in small pieces still moistened with rock-oil, and stirring with an iron rod. Combination then takes place, attended with evolution of heat and inflammation of the rock-oil (the gases evolved by which protect the alloy from oxidation). When the action is completed, the crucible is filled with warm sand and left to cool slowly; the crystalline alloy is pulverised in a warm mortar, with addition of a small quantity of dry sand, then introduced into a number of small flasks and drenched with iodide of ethyl, and the flasks are immediately connected with a condensing tube, to prevent loss of iodide of ethyl, which distils over in consequence of the heat evolved by the violent action which immediately takes place. The iodide of ethyl is allowed to flow back into the flasks as long as any action goes on, and when it is completed the excess of iodide of ethyl is distilled off over the water-bath; the remaining liquid is poured out of the flasks into a dry glass cylinder and shaken up with ether, which dissolves the plumbotriethyl; and the ether is distilled off after addition of a little water: the plumbotriethyl then separates as an oil at the bottom of the water.

Plumbotriethyl is a yellowish mobile oil, of specific gravity 1·471 at 0°, insoluble in *water*, easily soluble in *alcohol* and *ether*. It volatilises undecomposed in small quantity with ether-vapour, but cannot be distilled alone. By the action of light, or by prolonged boiling with water, it decomposes, with separation of metallic lead (Klippel). When exposed to the air in ethereal solution, it is converted into oxide (Löwig), carbonate (Klippel). *Chlorine-water* decomposes it, with separation of chloride of lead. (Klippel.)

Bromide of plumbotriethyl, $PpbE^3Br$, is obtained by adding an alcoholic solution of bromide of potassium to a solution of the sulphate in alcohol containing sulphuric acid, agitating the whole with ether, then with water to separate the ethereal solution, and evaporating the ether; it then crystallises in long needles. (Löwig.)

The *chloride*, $PpbE^3Cl$, is obtained by adding chloride of barium to a solution of the sulphate in alcohol containing hydrochloric acid, agitating with ether, separating the ethereal solution by water, and leaving it to evaporate (Löwig); by neutralising the oxide or carbonate with hydrochloric acid (Klippel); or by the action of hydrochloric acid gas on plumbotetrethyl (Buckton, p. 563). It crystallises in beautiful long needles, having a high lustre, and giving off a strong odour of oil of mustard when gently heated. When heated in a glass tube, they detonate slightly, even at a moderate heat, yielding chloride of lead and metallic lead. (Löwig.)

The *chloromercurate*, $\mathrm{PpbE^3Cl.HhgCl^2}$, separates from a hot alcoholic solution of the component salts in white nacreous scales; the *chloroplatinate*, $\mathrm{2PpbE^3Cl.PptCl^4}$, in copper-red crystals, sparingly soluble in water, more easily in alcohol and ether. (Klippel.)

The *cyanide*, $\mathrm{C^7H^{15}NPb^2 = PpbE^3Cy}$, is obtained by heating cyanide of potassium with an alcoholic solution of chloride of plumbotriethyl, for a considerable time, in a sealed tube placed in a water-bath, mixing the resulting blood-red liquid with water, and recrystallising the resulting white precipitate from ether. It then separates in prismatic crystals, which, when heated in a tube, melt and decompose, with deflagration, separation of metallic lead, and evolution of inflammable vapours. (Klippel.)

The *iodide*, $\mathrm{PpbE^3I}$, formed by the action of iodine on plumbotriethyl (Klippel), or by the reaction of iodide of potassium and sulphate of plumbotriethyl (Löwig), is soluble in ether and very unstable, the ethereal solution quickly yielding a deposit of iodide of lead.—If the compound, while yet undecomposed, be distilled with water, iodide of lead separates immediately, and the water which passes over is accompanied by a colourless, mobile, very pungent liquid, no longer prone to spontaneous decomposition, and having nearly the composition $\mathrm{(PpbE^3)^4I^3}$. (Löwig.)

Oxide of plumbotriethyl is obtained in the hydrated state by adding a solution of nitrate of silver mixed with alcohol to the alcoholic solution of the mixed radicles as long as metallic silver is precipitated; filtering from the silver; agitating the resulting solution of nitrate of plumbotriethyl with alcoholic potash and afterwards with ether; adding a sufficient quantity of water to separate the ethereal solution of the oxide; and evaporating the ether in a retort. Hydrated oxide of plumbotriethyl then remains in the form of a thick oily liquid, which solidifies after a while in a crystalline mass, slippery to the touch, like hydrate of potassium (Löwig). It may also be prepared by gradually adding iodine to the ethereal solution of plumbotriethyl till the colour no longer disappears, and immediately agitating the liquid with moist oxide of silver. An alkaline solution is thus obtained which, on addition of water and removal of the alcohol and ether by distillation, deposits hydrate of plumbotriethyl as a nearly colourless thickish oil (Klippel). It is volatile, and forms white fumes when a rod moistened with hydrochloric acid is held over it. When heated, it gives off white vapours, which excite powerful sneezing—a property which also belongs to the radicle itself and many of its compounds. The hydrate dissolves sparingly in water, readily in alcohol and in ether; has a strong alkaline reaction, and a sharp, disagreeable, caustic taste (Löwig, Klippel); saponifies fats; precipitates the oxides of iron, copper and silver from their salts; also alumina and oxide of zinc, both of which it redissolves when added in excess. (Klippel.)

Oxygen-salts. The oxide unites readily with acids, forming crystallisable salts.

The *acetate*, *benzoate*, and *butyrate* form needle-shaped crystals, soluble in water, alcohol, and ether.

Carbonate, $\mathrm{(PpbE^3)^2CO^3}$.—The hydrated oxide rapidly absorbs carbonic acid from the air, and by leaving the alcoholic solution to evaporate in the air, the carbonate is obtained in small hard crystals (Löwig), or it may be prepared by passing carbonic anhydride into the solution, and separated by addition of carbonate of ammonia, care being taken however to avoid an excess of the latter, which would give rise to the formation of an easily soluble double salt. Carbonate of plumbotriethyl has a strong burning taste, is nearly insoluble in water, sparingly soluble in alcohol and ether. Alcohol containing hydrochloric acid dissolves it with effervescence. (Löwig.)

Formate of plumbotriethyl resembles the acetate.

The *nitrate*, $\mathrm{PpbE^3.NO^3}$, is obtained by decomposing the alcoholic solution of the mixed plumbethyls (Löwig, p. 561), or the ethereal solution of pure plumbotriethyl (Klippel) with nitrate of silver. It remains on evaporation as a colourless, viscid liquid, which smells like butter, has a burning taste, and solidifies after a while to a crystalline unctuous mass. It is decomposed by heat, with slight detonation. It dissolves readily in alcohol and ether; the alcoholic solution when evaporated, deposits a small quantity of nitrate of lead. (Löwig.)

The neutral *oxalate* forms scaly laminar crystals, which when dried over oil of vitriol, contain $\mathrm{C^2(PpbE^3)^2O^4.H^2O}$. (Klippel.)

A *phosphate* $\mathrm{(PpbE^3)H^2PO^4}$, is obtained, by saturating the oxide or carbonate with phosphoric acid, in stellate groups of crystals which dissolve readily in water, alcohol, and ether, and are oxidised with vivid deflagration, when treated in the dry state with fuming nitric acid. (Klippel.)

Sulphate. $(PpbE^3)^2SO^4$.—When sulphuric acid is added by drops to an alcoholic solution of the oxide, leaving the base in excess, a dazzling white crystalline precipitate of the sulphate is obtained, which must be washed with alcohol and afterwards with ether. The salt is nearly insoluble in water, absolute alcohol, and ether, but dissolves readily in alcohol mixed with sulphuric or hydrochloric acid. From the acid solution it crystallises in tolerably large, hard, shining octahedral crystals (Löwig). Klippel, by dissolving the carbonate in alcoholic sulphuric acid, obtained the sulphate in crystals like those of quartz. Buckton, by decomposing the chloride with sulphuric acid or sulphate of silver, obtained it in asbestiform needles.

The *acid tartrate*, $C^4H^5(PpbE^3)O^6$ (at 100°), forms scaly laminar crystals.

Sulphide of plumbotriethyl is obtained by treating a solution of the oxide or a salt of plumbotriethyl, with sulphydric acid or sulphide of ammonium, as a white precipitate, which is nearly insoluble in water, alcohol, and ether, and blackens quickly with separation of sulphide of lead. (Klippel.)

The *sulphocyanate* is formed by heating an alcoholic solution of the chloride with recently precipitated sulphocyanate of silver to 100° in a sealed tube. It dissolves in water, alcohol, and ether, and crystallises from the ethereal solution in the same form as sulphocyanate of potassium. (Klippel.)

Plumbotetrethyl. $Pb^2C^8H^{20} = Ppb(C^2H^5)^4$ or $PpbE^4$. *Diethylide of lead. Plumbodiethylide* (Buckton).—Produced by the action of zinc-ethyl on chloride of lead:

$$2ZnE^2 + 2PpbCl^2 = 2ZnCl^2 + PpbE^4 + Ppb.$$

When dry chloride of lead is added to zinc-ethyl, decomposition takes place immediately, attended with separation of metallic lead, and slight rise of temperature; and on adding an excess of the lead-chloride, and warming gently for a few minutes, a clear liquid may be decanted, apparently consisting of several lead-radicles combined with zinc-ethyl, which cannot be completely removed by digestion with excess of lead-chloride, but may be expelled for the most part by distillation. The liquid remaining in the retort at 140°–150° yields, when treated with water and hydrochloric acid, heavy colourless drops of a liquid, the greater part of which, consisting of plumbotetrethyl, distils over between 198° and 202°; but the compound is most easily obtained in the pure state by distillation in a rarefied atmosphere. (Buckton.)

Plumbotetrethyl is a transparent colourless liquid of specific gravity 1·62. Under the ordinary pressure it boils with partial decomposition, at a few degrees above 200°, but under a pressure of 7·5 inches of mercury it boils without decomposition at 152°. When set on fire, it burns with pale-green-bordered flame, emitting a fume of lead-oxide. In a stream of hydrochloric acid gas, it is converted into chloride of plumbotriethyl, with evolution of hydride of ethyl:

$$Ppb(C^2H^5)^4 + HCl = Ppb(C^2H^5)^3Cl + C^2H^5.H. \quad \text{(Buckton.)}$$

Methyl-compounds.

Plumbotrimethyl. $Pb^2C^3H^9 = Ppb(CH^3)^3 = PpbMe^3$.—This compound has not yet been obtained in the free state, but its salts are produced, with evolution of hydride of methyl, by treating plumbotetramethyl with acids: *e.g.* with hydrochloric acid, the reaction being precisely similar to that which takes place in the case of the corresponding ethyl compound, as represented by the equation just given.

Chloride of plumbotrimethyl, $PpbMe^3Cl$, thus obtained, separates from the solution on cooling in long needles very much like chloride of lead. If the boiling of the plumbotetramethyl with hydrochloric acid be too long continued, chloride of lead is apt to be formed.

Bromide of Plumbotrimethyl is somewhat more soluble than the chloride.

The *iodide*, $PpbMe^3I$, is obtained by adding iodine to plumbotetramethyl till the colour becomes permanent (iodide of methyl being probably formed at the same time:

$$PpbMe^4 + I^2 = PpbMe^3I + MeI).$$

The product is a white solid mass, mixed with yellow iodide of lead, sparingly soluble in water, easily in alcohol, and crystallising in long colourless needles, which may be sublimed. By distillation with caustic potash, it yields the hydrate of plumbotrimethyl, as a strong basic oil, smelling like oil of mustard, and solidifying in prismatic needles. (Cahours.)

Plumbotetramethyl. $Pb^2C^4H^{12} = Ppb(CH^3)^4 = PpbMe^4$.—Produced by the action of iodide of methyl on an alloy of 5 pts. lead and 1 pt. sodium, or better, by treating chloride of lead with zinc-methyl. It is a colourless, mobile liquid, having a camphor-like odour, insoluble in water, but soluble in alcohol and ether. It boils at 160°, decomposes at a few degrees above that temperature, but may be distilled without alteration in a gas which does not act upon it (Cahours). According to Buttlerow, however, it smells like strawberries or mould, not at all like camphor, boils at 100°,* and when free from zinc-methyl, may be distilled without decomposition in contact with air; in a sealed tube containing chlorocarbonate of ethyl, it may be heated to 200° without decomposition. Its vapour-density, determined by Gay Lussac's method, is 9·66 at 115°, and 9·52 at 130°; calculation = 9·25. It appears then that the compound is converted into a perfect gas at a temperature very little above its boiling point. (Buttlerow.)

Plumbotetramethyl, like the corresponding ethyl-compound, does not unite directly with *oxygen*, *chlorine*, or *iodine*, but is decomposed thereby, yielding compounds in which part of the methyl is replaced by the acting elements, but belonging to the same type as plumbotetramethyl itself; *e.g.* iodide of plumbotriethyl, $Pb(CH^3)^3I$, by the action of iodine. Treated with *acids*, it yields hydride of methyl and a salt of plumbotriethyl. (Cahours.)

LEAD-SOAPS. Lead-salts of the fat-acids. Common lead-plaster (p. 560) is a preparation of this kind.—Palmer in 1845 patented the preparation of a lead-soap for greasing the axles of railway carriages, &c. It is prepared by heating the impure oleic acid obtained from the manufacture of stearin-candles, and stirring litharge into it as long as the litharge is dissolved. Before use it is mixed with a certain quantity of oil or tallow.—A compound of lead-oxide with the acids of linseed-oil, prepared by decomposing the potash-soap of linseed-oil with solution of acetate of lead, serves, when dissolved in oil of turpentine, for printing on wall-paper, previous to gilding it with gold-leaf or Dutch metal, or dusting it with wool-shearings for the production of flock-patterns.

LEAD-SPEISS. The metallurgical name of certain products obtained in the working of lead-ores containing arsenic or antimony. The following table exhibits the composition of two lead-speisses analysed by Bodemann: *a*, from Clausthal; *b*, from Andreasberg, and another; *c*, by Ahrend from the Lower Hartz:

	Pb	As	Sb	Cu	Ag	Fe	S	Co and Ni.
a.	68·2	. .	30·3	trace	. .	trace	1·5	
b.	90·5	0·1	1·3	0·3	0·1	2·6	5·0	
c.	26·1	13·0	5·2	44·5	0·1	5·5	2·8	2·3

LEAD-VITRIOL. Sulphate of lead (see SULPHATES).

LEAF-GREEN. See CHLOROPHYLL (i. 922).

LEAF-RED. See ERYTHROPHYLL (ii. 506).

LEAF-YELLOW. See XANTHOPHYLL.

LEATHER consists of the skins of animals prepared by a process, or rather series of processes, called tanning, by which they are preserved from putrefying while moist, and rendered soft and pliable when dry. The skins are first freed from epidermis, fatty matter and hairs, by steeping them in milk of lime, or in an acescent infusion of barley- or rye-meal, or spent tan, which sets up a slow fermentation; by either of these modes of treatment, the epidermis and the cellular tissue in which the hairs are rooted, are disintegrated, so that the hair and epidermis can then be easily removed by scraping. The skins thus prepared are then steeped in an infusion of some substance capable of uniting with the true skin and converting it into leather. The materials used for this purpose are:

1. *Tannin* or *tannic acid*, in the process of tanning properly so called, which is applied chiefly to the stouter kinds of leather, made from the hides of oxen and horses. The true skin of animals is a gelatinous tissue (ii. 826) and gelatin unites with tannic acid, forming a tough insoluble substance possessing the properties of leather (ii. 765). Several substances are used by the tanner as sources of tannic acid; but the most valuable and most extensively used of all is oak-bark. The following substances are also used, sometimes alone, but more generally as additions to the oak-bark:—Sumach, from the bark of *Rhus cotinus* or *Rhus coriaria*; catechu, or *Terra Japonica*, chiefly from various species of *Acacia* (i. 816); dividivi, the crushed pods of *Cæsalpinia coriaria*; mimosa, from the bark and pods of various kinds of *Prosopis*, a genus of leguminous plants; valonia, the acorn of the great prickly-cupped oak (*Quercus Ægilops*); and nut-galls.

2. *Alum* and *common salt*, in the process called tawing, which is applied chiefly to the lighter kinds of skin, namely these of sheep, goats, and calves.

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* This boiling point differs from that of plumbotetrethyl (about 200°) by 90°, or 22·5° for a difference of CH^2 in the formulæ, whereas the boiling point of plumbotetramethyl found by Cahours, viz. 160°, differs from 200 by only 40°, or by 10° for each difference of CH^2 in the formulæ. Now on comparing the differences of boiling points in the corresponding methyl- and ethyl-compounds of phosphorus, arsenic, antimony, and tin, it is found that the difference always amounts to 20° or upwards for each molecule of CH^2 added to the compound. The boiling point of plumbotetramethyl found by Buttlerow is therefore more in accordance with analogy than that determined by Cahours.

3. *Oil*, for the preparation of **chamois, shamoy,** or **wash-leather**, which is prepared from the skins of the goat, doe, or chamois, and is a soft, spongy leather, capable of washing.

4. *Lime*, for **parchment**, which is prepared from calf or sheep skins, and for the stronger kinds, from asses' or pig's skin.

For the details of all these processes we must refer to *Ure's Dictionary of Arts, &c.* (ii. 674—686), and the *Handwörterbuch der Chemie* (iv. 792—810).

LECANORIC ACID. $C^{16}H^{14}O^7$? *Lecanorin. a-Orsellic acid.* (Schunck, Ann. Ch. Pharm. xli. 157; liv. 261; lxi. 72.—Rochleder and Heldt, *ibid.* lxviii. 1.—Stenhouse, *ibid.* lxviii. 61; lxx. 218.—Strecker, *ibid.* lxviii. 13.—Laurent and Gerhardt, Ann. Ch. Phys. [3], xxiv. 315.—Robiquet, Ann. Ch. Phys. xlii. 236; Gm. xii. 377.)—This substance, which was discovered by Schunck in 1842, is extracted from several lichens belonging to the genera *Lecanora* and *Variolaria*. The lichens, in the state of fine powder, are exhausted with ether in a percolator, and, on evaporating the ether, a residue is obtained which is to be washed with ether on a large funnel till it is colourless, then exhausted with water, and crystallised from alcohol (Schunck). Rochleder and Heldt exhaust the lichen (*Evernia prunastri*) with a mixture of ammonia and alcohol, dilute the alcohol with a third of its volume of water, and saturate with acetic acid. Lecanoric acid then separates in grey flocks, which are washed, dried at 100°, dissolved in a small quantity of boiling absolute alcohol, and purified by recrystallisation.

Stenhouse macerates the lichen (*Roccella tinctoria*) with water mixed with slaked lime, precipitates the filtered liquid with hydrochloric acid; washes and dries the gelatinous precipitate, and digests it, when nearly dry, with absolute alcohol, taking care not to boil the liquid, which, on cooling, deposits the acid in crystals.

Lecanoric acid crystallises in colourless stellate needles, sparingly soluble in cold *water* and in cold *alcohol;* moderately soluble in boiling alcohol, soluble in *ether* and in *acetic acid*. According to Schunck, 1 pt. of lecanoric acid requires for solution 2,500 pts. of boiling water, 150 pts. of alcohol of 80 per cent. at 15°; 5·15 pts. of boiling alcohol, and 80 pts. ether at 15·5°. The solution reddens litmus. The crystallised acid does not lose weight at 100°.

Lecanoric acid gives by analysis 59·45 to 60·59 carbon, and 4·40 to 5·00 hydrogen, whence Stenhouse deduced the formula $C^{16}H^{16}O^7$, which Gerhardt altered to $C^{16}H^{14}O^7$ (60·37 per cent. C, 4·40 H, and 35·23). This latter formula readily explains the conversion of lecanoric into orsellic acid (*infra*).

Lecanoric acid yields by dry distillation, a viscid oil, together with orcin. It dissolves readily at ordinary temperatures in lime-water or baryta-water, and is precipitated therefrom by acids in the form of a jelly, and without alteration; but if the saturated solution be boiled, the lecanorate of barium or calcium changes into the much more soluble *orsellinate*. If the ebullition be prolonged, carbonate of barium or calcium is precipitated, and *orcin* remains in solution:

$$\underset{\substack{\text{Lecanoric}\\\text{acid.}}}{C^{16}H^{14}O^7} + H^2O = \underset{\substack{\text{Orsellinic}\\\text{acid.}}}{2C^8H^8O^4} = 2CO^2 + \underset{\text{Orcin.}}{2C^7H^8O^2}.$$

A solution of lecanoric acid in aqueous *ammonia* acquires by exposure to the air a fine purple colour, due to the formation of orcein. In contact with *hypochlorite of calcium*, lecanoric acid immediately assumes a red tint, quickly changing to brown and yellow. The acid heated with *sulphuric acid*, is gradually converted into **orcin**. Boiling *nitric acid* converts it into oxalic acid. Boiling *acetic acid* dissolves it readily, and deposits it in small needles on cooling. By boiling with *alcohol*, it is converted into orsellate of ethyl. The same change is produced by passing hydrochloric acid gas into a solution of lecanoric acid in absolute alcohol, saturated at the boiling heat.

The ammoniacal solution of lecanoric acid forms white precipitates with basic *acetate of lead* and *nitrate of silver*; but the silver precipitate is quickly reduced. The alcoholic solution gradually produces, with an alcoholic solution of *acetate of copper*, a light apple-green precipitate. It does not precipitate the alcoholic solutions of neutral acetate of lead, mercuric chloride, chloride of gold or nitrate of silver. A few drops of *ferric chloride* impart to it a deep purple colour.

The **lecanorates** gradually decompose, especially when heated, yielding orsellinic acid, and ultimately orcin. The *barium-salt*, $C^{16}H^{12}BaO$, is obtained by dissolving the acid in cold baryta-water, passing carbonic acid into the liquid, and treating the precipitate with alcohol, which dissolves the lecanorate of barium, and deposits it in small stellate needles. According to Stenhouse's analysis, it contains 49·27 per cent. C, 3·81 H, and 19·49 baryta; the formula requires 49·87 C, 3·37 H, and 19·73 baryta. The *calcium-salt* is a gelatinous precipitate, slightly soluble in water and alcohol, obtained by mixing an ammoniacal solution of the acid with chloride of calcium. The *lead-salt* is precipitated, according to Rochleder and Heldt, on mixing the boiling alcoholic solutions of lecanoric acid and acetate of lead; the precipitate thus obtained probably consists for the most part of orsellinate.

LECANORIN. Syn. with LECANORIC ACID.

LECITHIN. Gobley's *Matière visqueuse.* (Gobley, J. Pharm. [3] ix. 1, 83, 161; xi. 409; xii. 5; xvii. 401; xviii. 107; xix. 406; xxi. 241; xxx. 241; xxxiii. 161.)—The eggs and milt or soft roe of the carp and herring, the yolk of poultry-eggs, the brain of the domestic fowl, of man and of the sheep, venous blood, ox-bile, and the fat of the garden-snail, contain, together with cholesterin, olein and margarin, a viscous substance which is decomposed by boiling with acidulated water, yielding cerebrin, oleic acid, margaric acid and phosphoglyceric acid (ii. 891). Of these products, Gobley regards the cerebrin as adventitious, the other three as resulting from the decomposition of a non-isolable substance, *lecithin.* The portion of pig's bile soluble in alcohol and not precipitable by ether contains, besides cholesterin and ordinary fats, a phosphoretted fat corresponding with Gobley's lecithin, and resolvable by boiling with baryta-water into phosphoglycerate of barium and insoluble barium-salts (Strecker, Ann. Ch. Pharm. cxxiii. 356). A constituent of yolk of egg, resembling ear-wax, described by Kodweiss (Ann. Pharm. lix. 261), agrees also in properties with the substance described by Gobley.

When carps' eggs are exhausted with ether or boiling alcohol, and the solution is evaporated, there remains a reddish-yellow soft mass, which when redissolved in boiling alcohol, leaves a small quantity of oil, and separates again as a viscous mass on cooling. It may also be obtained in the same manner, but less pure, from yolk of egg (ii. 364).—When the comminuted and partially dried milt of the carp is shaken up with ether, the ether takes up the greater part of the viscous matter, and the rest may be obtained by repeated boiling with alcohol. On evaporating the alcoholic solution, transferring the viscous matter contained in the residue to ether by agitation therewith, and evaporating the ether, the viscous matter is obtained free from the salts taken up by the alcohol, which remain in the lower watery layer of liquid.

The viscous matter is colourless, or has merely a faint yellow or orange tint; it is soft, neutral, and has for the most part the odour of the material from which it has been prepared. It is frequently contaminated with earthy phosphates and albumin. It swells up when *heated*, chars without melting, gives off ammoniacal vapours, and leaves an acid carbonaceous residue containing phosphoric acid. When exposed to the *air*, it does not turn acid, and afterwards yields the same decomposition-products as that which has been prepared without exposure to the air. When shaken up with *water*, it forms an emulsion which does not become sour or exhibit the presence of phosphoglyceric acid, even after 12 hours' boiling, but on boiling it with water containing *sulphuric* or *hydrochloric acid*, oleic and margaric acids are formed, which rise to the surface as an oil, and phosphoglyceric acid, which remains dissolved in the water. Addition of alcohol accelerates this decomposition, which, in viscous matter from yolk of egg, takes place at the mere heat of the water-bath, but in that derived from other sources, not till after half an hour's actual boiling. The oxygen of the air has no influence on the decomposition. Besides the products above mentioned, there are obtained cerebrin, and sometimes also cholesterin, olein and margarin, which however are regarded by Gobley as accidental admixtures.—Aqueous *alkalis* and *alkaline carbonates* at the boiling heat produce the same decomposition as the mineral acids. When the viscous matter of yolk of egg is shaken up with water containing potash and heated in the water-bath, acetic acid separates oleic and margaric acids from it; with the viscous matter of the brain or from any other source, boiling with alcoholic potash is necessary to effect the decomposition. Carbonate of potassium also does not decompose the viscous matter merely at the heat of the water-bath, but only on actual boiling.—Six hours' boiling with *acetic* (lactic or tartaric) acid does not produce any decomposition, 12 hours' boiling only an imperfect decomposition of the viscous matter; but by 24 hours' boiling, it is completely decomposed, with formation of phosphoric acid and glycerine. (Gobley.)

From the emulsion formed by *water*, which froths like soap (Gobley), it is precipitated by common salt. (Kodweiss.)

The viscous matter dissolves sparingly in cold, easily in boiling *alcohol;* it is also soluble in *ether.* (Gobley.)

LECONTITE. This name is given by W. H. Taylor (Sill. Am. J. [2]. xxvi. 273) to an alkaline sulphate, found by Le Conte in the cavern of Las Piedras, near Comayagua in Honduras, and probably formed from the excrements of bats, which frequent the cavern in large numbers. The mineral, when freed from adhering organic matter, is colourless, permanent in the air, and has a saline, bitter taste. It forms prismatic crystals, which, according to Dana, are trimetric combinations,

$oP . \infty P . \infty \breve{P}2 . \frac{1}{4} \bar{P}\infty . \infty \bar{P}\infty$. Angle $\infty P : \infty P = 103° 12'$; $\infty \breve{P}2 : \infty \breve{P}2 = 115°$; $\frac{1}{4}\bar{P}\infty : \frac{1}{4}\bar{P}\infty$ over the principal axis = 127° 30′ to 128°. Hardness = 2 to 2·5. According to Taylor's analysis, it contains 12·94 per cent. $(NH^4)^2O$, 2·67 K^2O, 17·56 Na^2O, 44·97 SO^3, 19·45 water, 2·30 organic residue, and a trace of phosphoric acid, agreeing with the formula $M^2SO^4.H^2O$.

The form of this substance agrees essentially with that assigned by Mitscherlich (Pogg. Ann. lviii. 469) to the salt $\left.\begin{matrix}NH^4\\Na\end{matrix}\right\}SO^4.2H^2O$. (Jahresber. 1858, p. 729.)

LEDERERITE. A mineral from Cape Blomidon, Nova Scotia, having the form of gmelinite (ii. 924) and the same formula, but with only one-third the amount of water. Specific gravity = 2·169. Analysis by Hayes (Sill. Am. J. [2], xxv. 78): 49·47 per cent. SiO^2, 21·48 Al^4O^3, 11·48 Ca^2O, 3·94 Na^2O, 0·14 Fe^2O, 3·48 P^2O^5, and 8·58 water (= 98·57).

LEDERITE. Syn. with SPHENE.

LEDITANNIC ACID. $C^{28}H^{30}O^{15}$? (E. Willigk, Ann. Ch. Pharm. lxxiv. 363.—Rochleder and Schwartz, *ibid.* 366.)—A variety of tannic acid, obtained from the leaves of the marsh wild rosemary (*Ledum palustre*). It is prepared by precipitating the alcoholic decoction of the leaves with water, after distilling off the alcohol; precipitating the filtrate with neutral acetate of lead; dissolving the precipitate in dilute acetic acid; filtering again, precipitating the filtrate at the boiling heat with basic acetate of lead; decomposing the precipitate under water with sulphydric acid; and evaporating the filtrate in a stream of carbonic anhydride (Rochleder and Schwartz). Leditannic acid then remains as a reddish inodorous powder, easily soluble in water and in alcohol. The aqueous solution is coloured dark-green by ferric chloride, and forms yellow precipitates with acetate of lead and stannic chloride.

LEDIXANTHIN. A yellow or red pulverulent substance, produced by boiling aqueous leditannic acid with sulphuric or hydrochloric acid. According to Willigk, it contains $C^7H^6O^3$, and is therefore produced from leditannic acid by elimination of water: $C^{28}H^{30}O^{15} - 3H^2O = 4C^7H^6O^3$. It dissolves easily in alkalis, and when dissolved in alcohol, forms a red-brown precipitate with an alcoholic solution of neutral acetate of lead. By dry distillation, it yields an oil and crystals of pyrocatechin. (Willigk.)

LEDUM, OIL OF. The statements of different observers respecting this oil, which is obtained by distilling the leaves of *Ledum palustre*, or the entire plant at flowering time, with water, exhibit considerable diversities. According to Willigk (Wien. Akad. Ber. ix. 302), it consists for the most part of a hydrocarbon isomeric with oil of turpentine, and of an oxygenated oil, $C^{50}H^{128}O^{5}$. According to Grassmann (Repert. Pharm. xxxviii. 53), it consists of 1 pt. volatile oil and 2 pts. camphor or stearoptene, which may be separated by slow distillation, the volatile oil passing over first. The camphor forms colourless, slender, transparent prisms, which melt at a gentle heat, and sublime at a stronger heat, diffusing a pungent odour, which produces head-ache and giddiness. The camphor consists, according to Buchner (J. Pharm. [3] xxix. 318), of a hydrocarbon isomeric with oil of turpentine, and a hydrate of that hydrocarbon, $C^{50}H^{86}O^3 = 5C^{10}H^{16}.3H^2O$. It is nearly insoluble in water, dissolves easily in hydrochloric acid, less in acetic acid, and is quite insoluble in aqueous ammonia, but dissolves readily in alcohol and ether. (Buchner.)

According to A. Fröhde (J. pr. Chem. lxxxii. 181), the oil obtained from the plant by distillation is reddish-yellow, has an acid reaction, smells like the flowering plant, is slightly soluble in water, easily in alcohol and ether, and does not deposit any solid camphor, even when cooled to a very low temperature. When heated with strong potash-ley, it gives up to the alkali, besides small quantities of acetic, butyric, and valerianic acids, an oily acid, having the penetrative odour of the plant, and consisting probably of $C^8H^{16}O^4$, a formula closely related to that of ericinone, $C^6H^6O^2$ (ii. 500), which substance likewise exists in the plant. The portion of the oil which does not unite with potash, yields, by rectification in a stream of hydrogen, a portion boiling at 160°, and isomeric with oil of turpentine, while between 240° and 242° an oxygenated oil passes over, having the composition of ericinol, $C^{10}H^{16}O$.

LEEDSITE. A mineral found near Leeds in Yorkshire, containing, according to Thomson's analysis, 71·9 per cent. sulphate of calcium and 28·1 sulphate of barium. It appears to be merely a mechanical mixture of the two. (Dana, ii. 507.)

LEEK. The bulbs of this plant yield 0·46, the stems 0·84 per cent. ash, containing, according to T. Richardson (Ann. Ch. Pharm. lxvii., Appendix to Part 3):

	K^2O	Na^2O	Ca^2O	Mg^2O	SO^3	SiO^2	P^2O^5	Ferric phosphate.	NaCl		
Bulb .	32·35	8·04	12·66	2·70	8·34	3·04	15·09	13·29	4·49	=	100·00
Stem .	13·98	14·43	25·10	trace	16·50	19·77	. .	10·06	trace	=	99·84

LEELITE. Syn. with HELLEFLINTA (p. 141).

LEGUMIN, or *Vegetable Casein*, was discovered by Einhof in 1805, and was called by him *végéto-animale* (N. allgem. J. d. Ch. v. A. Gehlen, vi. 126, 548). He found it in peas, beans, and lentils. A similar nitrogenised substance, extracted from sweet and bitter almonds and termed *amandin*, has been investigated by Proust, H. Vogel, Boullay, and others, who considered the substance in question to be identical with animal casein. Braconnot, and afterwards Liebig, have arrived at the same result; they find, indeed, that legumin and casein are perfectly identical in composition and properties. Dumas and Cahours on the other hand, always obtained a substance containing less carbon and more nitrogen than casein, and possessing somewhat different properties. Their analyses agree very closely with one another, but it is highly probable that the substance analysed contained some foreign body, perhaps arising from the partial decomposition of legumin. It is also not unlikely that legumin prepared by the ordinary methods is not a homogeneous substance.

Preparation.—Dumas and Cahours employ the following method for the preparation of legumin, the most advantageous source of which are peas or sweet almonds:—The bruised substance is digested for two or three hours with tepid water; the product is then crushed in a mortar so as to form a pulp; and to this is added about its own weight of cold water. After the whole has been macerated for an hour, it is thrown on a cloth and pressed, and the liquid portion on standing deposits a certain quantity of starch. The solution is now clarified by filtration, and acetic acid, diluted with 8 or 10 times its weight of water, is gradually added. Immediately on the addition of the acid, a perfectly white flocculent precipitate is formed, which may be easily collected on a filter and washed with water. Care must be taken to avoid an excess of acetic acid, in which legumin is readily soluble. The legumin is then washed with alcohol, dried, pulverised, and digested with ether, which removes all fatty matters. The product is again dried in vacuo at 140° (Gerhardt, *Traité*, iv. 491). Haricot-beans cannot well be substituted for the above substance, since they contain a gummy matter which renders the filtration and washing exceedingly tedious. According to Löwenberg, the product, obtained as above, is a mixture of legumin and albumin, and after it has been washed with boiling water, contains a decomposition-product of legumin, mixed with albumin. The separation of these two substances may be effected by dissolving the mixture in ammonia, evaporating off the excess of ammonia, adding chloride of sodium, boiling, filtering, and precipitating the filtrate with acetic acid. The precipitate is washed first with cold water, then with boiling alcohol and ether. The infusion of peas and almonds also contains a third body, which is precipitated by acetic acid; it is insoluble in excess of the acid, but soluble in pure water. The ammoniacal solution is partly precipitated by boiling with chloride of sodium after evaporating the excess of alkali.

Rochleder purifies legumin, prepared by the first method, by treating it with concentrated potash, which readily dissolves the legumin, and leaves a flocculent residue of another substance. The solution is allowed to stand, decanted, then filtered and precipitated by acetic acid. The well-washed precipitate is dissolved in ammonia, filtered again, and reprecipitated by acetic acid.

Properties.—The solution of legumin does not coagulate by ebullition; but when evaporated, becomes covered with a pellicle, like milk (Liebig). Purified legumin is insoluble in cold water; with boiling water it yields a product richer in carbon, soluble in water and insoluble in acetic acid, together with a less carbonised body, insoluble in water (Löwenberg). The body analysed by Dumas and Cahours had the following properties:—When precipitated from a concentrated solution by weak acetic acid, it always presented a nacreous and iridescent appearance; from a weak solution it is deposited in flakes. It is insoluble in cold alcohol and ether; also in boiling water and in weak boiling alcohol. It dissolves largely, however, in cold water, and when the liquid is heated almost to boiling, it coagulates, and gives a precipitate of cohering flakes very like coagulated albumin (Gerh. iv. 493). Gerhardt thinks that Liebig may have experimented with the aqueous extract of legumin obtained directly from peas, &c., which probably contains that substance in combination with alkali, forming an incoagulable solution like the alkaline albuminates. The fresh aqueous extract of the fruit of the leguminosæ is always neutral; the legumin precipitated therefrom by an acid always reddens litmus, even after prolonged washing. When this solution is left to itself, it coagulates in 24 hours, at a temperature of 15 or 20° C., yielding a gelatinous precipitate like the coagulum of milk. The mother-liquor is decidedly acid, and appears to contain lactic acid. (Liebig.)

In the following analyses the ash is deducted:—

	Dumas and Cahours.[*]		Rochleder.[†]			Rülling.[‡]	Löwenberg.[‖]
	Lentils.	*Sweet almonds.*	*Haricots.*			*Peas.*	*Peas.*
Carbon . .	50·46	50·93	54·0	54·3	53·9	50·68	53·9
Hydrogen .	6·65	6·70	7·5	7·4	7·3	6·74	7·2
Nitrogen . .	18·19	18·77	14·7	14·6	15·0	16·50	
Sulphur . .	. .	. .	. .	. .	. .	0·48	0·3
Oxygen . .							

Purified legumin sometimes contains as much as 7·1 per cent. ash (Rochleder). The ash is perfectly white, has an alkaline reaction, and contains a large quantity of potash, partly in combination with phosphoric acid. The insoluble portion of the ash is composed of phosphate of calcium and magnesium, as well as a little phosphate of iron. (Liebig.)

Völcker (Rep. Brit. Assoc. 1857, pr. 60; J. p. Chem. lxxv. 320) found in legumin prepared from peas and beans, the following percentage of ash, phosphorus, and sulphur:

Legumin.	Ash.	Phosphorus.	Sulphur.
From green peas	1·100	1·383	0·870
The same, precipitated with a small quantity of acetic acid	. .	1·880	0·571
The same, precipitated with excess of acetic acid	.	2·180	0·851
From white peas	1·45	1·520	
From white French beans	0·71	1·780	0·590

Norton (Pharm. Centr. 1847, p. 466; 1848, p. 240) also found in legumin prepared from peas, sweet almonds, and oats, from 0·8 to 2·3 per cent. phosphorus. The large amount of phosphorus found by Völcker and Norton renders it probable that legumin contains, or is associated with, a compound of phosphoric acid, perhaps phosphoglyceric acid.

Decompositions.—When legumin is subjected to dry distillation, it swells, yields a yellowish distillate containing carbonate, sulphide, and acetate of ammonium, and leaves a residue of shining charcoal. (Braconnot.)

Legumin distilled with *acid chromate of potassium and dilute sulphuric acid* yields an acid liquid which smells of prussic acid and bitter almond oil, contains a considerable quantity of prussic acid, with a small quantity of formic acid, but does not give the reactions of the aldehydes with potash or with nitrate of silver. When rectified over mercuric oxide, the first portion of the distillate exhibited a more aromatic and ethereal odour than the original liquid; the second portion, which was covered with a thin layer of oil, contained benzoic acid (4 pts. to 1,000 of legumin) valerianic, butyric, propionic, acetic, caproic, and probably also caprylic acid (Fröhde, J. pr. Chem. lxxvii. 290). In a second series of experiments, Fröhde found among the products of oxidation of legumin, valeronitrile, acetonitrile (not distinctly recognised), and a third nitrile, probably propionitrile.

All *acids* coagulate the solution of legumin; the precipitates redissolve in excess of the acid.

When legumin is boiled with *dilute sulphuric acid*, leucine is formed. Dry legumin saturated with *concentrated sulphuric acid* dissolves slowly and forms a brown solution, but no glycocine is produced.

Concentrated *nitric acid* dissolves dry legumin, with evolution of nitrous fumes.

Dilute *hydrochloric acid* precipitates legumin like acetic acid. The concentrated acid dissolves it with the characteristic blue tint.

When gelatinous legumin is placed in contact with concentrated *acetic acid* it absorbs the acid, and swells, becoming semitransparent. The product is completely soluble in boiling water. A gummy residue of legumin, soluble in water, is obtained on evaporation. A solution of legumin is immediately precipitated by dilute acetic acid, and the precipitate is redissolved by an excess of the acid, forming a perfectly clear solution. This is reprecipitated by adding ammonia; the precipitate dissolves in an excess of the acid (Dumas and Cahours). Liebig found legumin insoluble in weak acetic acid; Löwenberg's legumin, which is insoluble in water, dissolves in an excess of acetic acid.

Solution of legumin is precipitated by tribasic *phosphoric acid*, also by *oxalic, tartaric, malic*, and *citric acids*; the precipitates are readily soluble in excess of acid. Legumin is dissolved in the cold by *potash, soda*, and *ammonia*. Heated with fixed alkali, it evolves ammonia, and sulphide of ammonium is formed in the solution.

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[*] The carbon and nitrogen in the other analyses of MM. Dumas and Cahours fall between these two analyses.

[†] Previously purified by Rochleder's method.

[‡] The substance was redissolved in ammonia, precipitated by acetic acid, and exhausted by boiling alcohol and ether.

[‖] Purified by Löwenberg's process.

Baryta and *lime* form insoluble compounds with legumin, as with casein. Like casein, solution of legumin precipitates many earthy and metallic salts, but does not precipitate sulphate of magnesium, or the acetate, or other salts of calcium in the cold; on applying a slight heat, the liquid rapidly coagulates. Braconnot attributes the hardening of vegetables cooked in selenitic waters to the formation of these lime-compounds.

A concentrated solution of legumin, to which rennet has been added, does not begin to coagulate for several hours; after 24 hours all the legumin is precipitated. The coagulation does not appear from this to be due to the free acid contained in the rennet (Dumas and Cahours). Putrefying legumin acts as a powerful ferment.

Dry beans, peas, lentils, &c., contain, on an average, about 25 per cent. of nitrogenised matter (legumin, albumin, &c.), and are the most nutritive of vegetables. At the same time, they are deficient in starch and fat. They are not generally a very wholesome food in large quantity, except for men enjoying robust health and engaged in severe labour. Legumin appears to be much more indigestible than insoluble casein, as casein is far more indigestible than the fibrin of meat. C. E. L.

LEHMANNITE. Native chromate of lead (i. 934).

LEHRBACHITE. Selenide of mercury and lead from Tilkerode, near Lehrbach; probably a mechanical mixture of the two selenides, inasmuch as specimens from different parts of the same vein exhibits very different proportions of lead and mercury (see p. 558).

LEHUNTITE. Syn. with NATROLITE.

LEIDENFROST'S PHENOMENON. This term is sometimes applied to the spheroïdal state of liquids (p. 88), first observed by Leidenfrost.

LEMNA. *Duckweed.*—Plants of this genus are very rich in inorganic substances, and have accordingly been recommended for use as manure. In a specimen of *Lemna minor* growing in the river Eure, in France, Hervé Mangon (Instit. 1861, p. 107) found:

Combustible matter (without nitrogen).	Nitrogen.	Silica.	Lime.	Phosphoric acid.	Other mineral constituents.
61·1	3·6	6·7	8·2	1·1	19·3 = 100

Liebig (Ann. Ch. Pharm. cv. 109) obtained from *Lemna trisulca* growing in a marsh, 16·6 per cent. ash, and from a litre of the surrounding water 0·415 grm. of saline residue. 100 pts. of the slightly ignited plant-ash, *a*, and of the saline residue of the water, *b*, contained:

	Ca^2O	Mg^2O	$NaCl$	KCl	K^2O	Na^2O	Fe^4O^3*	P^2O^5	SO^3	SiO^2
a.	16·82	5·08	5·90	1·45	13·16	. .	7·36	8·73	6·09	12·85
b.	35·00	12·26	10·10	. .	3·97	0·47	0·72	2·62	8·27	3·34

LEMNIAN EARTH. *Sphragide.*—The Λημνία σφραγὶς of the Greeks. A yellowish-grey earth or clay frequently marbled with rusty spots. Dull. Fracture fine earthy. Meagre to the touch. Adheres slightly to the tongue. When plunged in water it falls to pieces, with disengagement of air-bubbles. Its constituents are, 66 silica, 14·5 alumina, 0·25 magnesia, 0·25 lime, 3·5 soda, 6 oxide of iron, 8·5 water (Klaproth). It has hitherto been found only in the Island of Stalimene (ancient Lemnos). It is reckoned a medicine in Turkey; and is dug up only once a year, with religious solemnities, cut into spindle-shaped pieces, and stamped with a seal. In ancient times it was esteemed an antidote to poison and the plague. U.

LEMON. See CITRUS (i. 1003).

LENTIL. *Ervum Lens.* The air-dried seed of this leguminous plant contains, according to Krocken (Ann. Ch. Pharm. lviii. 224), from 34 to 35 per cent. starch. Horsford (*ibid.* 199) found in 100 pts. of the seed, 30·4 pts. of non-azotised matter, to 2·6 ash and 13·0 water.

Poggiale (J. Pharm. [3]. xxx. 180, 255), and Fresenius found in 100 pts. of air-dried lentils, the following constituents:

Starch.	Gum.	Sugar.	Legumin.	Fat.	Cellulose, Pectin, &c.	Ash.	Water.	
44		. .	29·0	1·5	7·7	2·4	15·4	Poggiale.
35·5	7·0	1·5	25·0	2·5	12·0	2·3	14·0	Fresenius.

Levi found in lentil-seeds from Worms 2·06 per cent. ash of the composition given below.

The straw of lentils contains 0·01 per cent. nitrogen (Boussingault); the air-dried straw contains 27 per cent. water and 34 per cent. substances soluble in dilute alkaline ley, 57 per cent. woody fibre, and 3·9 per cent. ash, having the following composition:

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* With traces of alumina.

Composition of Lentil-ash.

	Seed.	Straw.		Seed.	Straw.
Potash	34·6	10·8	Silica	1·3	17·6
Soda	9·5		Phosphoric acid . .	36·2	12·3
Lime	6·3	52·3	Sulphuric acid		1·0
Oxide of manganese .	2·5	3·0	Chloride of sodium .	7·6	2·1
Ferric oxide . . .	2·0	0·9			

According to Schwarz, a hectare of ground yields about 1,360 kilogrammes of seed and 3,700 kilogrammes of straw; the former, therefore, containing 30, the latter 144, and the whole, 174 kilogrammes of mineral constituents (Handb. d. Chem. ii. [3] 832).

LENZINITE. A variety of kaolin from the pegmatite of La Vilate near Chanteloupe (Haute Vienne), of a clear brown colour, tender, but not plastic. Before the blowpipe it becomes reddish, but does not fuse.. It is decomposed by hot sulphuric acid. Contains, according to Salvétat (Ann. Ch. Phys. [3] xxxi. 102), 36·36 per cent. silica, 36·00 alumina, 1·95 ferric oxide, and 21·50 water (agreeing nearly with the formula $2Al^4O^3.3SiO^2.3H^2O$), besides 0·18 magnesia, 0·50 alkalis, 2·0 gelatinous silica, and 1·64 quartz (= 101·62).

LEONHARDITE. A hydrated silicate of calcium and aluminium, occurring at Schemnitz in Hungary, and at Copper Falls, Lake Superior, in monoclinic crystals, in which ∞P : ∞P = 83° 30′ and 96° 30′; oP : ∞P = 114°. Cleavage parallel to ∞P, very perfect; basal imperfect. Also columnar and granular. Hardness = 3 to 3·5. Specific gravity = 2·25. Lustre on cleavage-faces pearly; elsewhere vitreous. Colour white, sometimes yellowish, seldom brownish. Subtranslucent. It usually whitens on exposure, like laumontite; but the variety from Lake Superior does not. Before the blowpipe it exfoliates, froths, and easily melts to an enamel. It dissolves in acids.

Leonhardite from Schemnitz has been analysed by Delffs and v. Babo (Pogg. Ann. lix. 336, 339), that from Copper Falls by Barnes (Sill. Am. J. [2] xv. 440):

	Schemnitz.		Copper Falls.
Silica	54·92	55·00	55·50
Alumina . . .	22·49	24·36	21·69
Lime	9·05	10·50	10·56
Water	13·54	12·30	11·93
	100·00	102·16	99·68

The analyses do not agree well together. The first analysis of the Hungarian mineral agrees approximately with the formula $(3Ca^2O.4SiO^2).4(Al^4O^3.3SiO^2) + 15H^2O$, which, however, is improbable; that of the American mineral may be represented by the much simpler formula $(Ca^2O.SiO^2).(Al^4O^3.3SiO^2) + 3H^2O$, or $2CaAl\!l''Si^2O^6.3H^2O$, which is that of a metasilicate, and differs from the formula of laumontite (p. 472) only in the amount of water. According to Brooke and Miller, leonhardite agrees in form also with laumontite. Delffs found in the mineral 13·55 to 13·81 per cent. water; it gave off 11·64 per cent. at 100°. According to Kenngott, leonhardite is identical with caporcianite. (Dana, ii. 308; Rammelsberg, *Mineralchemie*, p. 806.)

LEOPARDITE. A spotted felspathic rock, occurring at Charlotte, Mecklenburgh County, and in the Steele Mine, Montgomery County, North Carolina, and recognised by Genth (Sill. Am. J. [2] xxxiii. 197), as a true porphyry, spotted with iron- and manganese-compounds. The crypto-crystalline felspathic base is interspersed with small crystals of orthoclase and quartz. Analysis gave:

SiO^2	Al^4O^3	Fe^4O^3	Mg^2O	Ca^2O	Na^2O	K^2O	Loss by ignition.	
75·92	14·47	0·88	0·09	0·02	4·98	4·01	0·64	= 100·00

agreeing very nearly with the composition of Bunsen's normal trachytic substance.

LEPAMINE. A volatile base containing the elements of 1 at. diamylamine and 1 at. lepidine; $C^{10}H^{23}N.C^{10}H^9N = C^{20}H^{32}N^2$, produced by the action of iodide of amyl on lepidine (p. 573).

LEPARGYLIC ACID. Syn. with ANCHOIC ACID (i. 289). Arppe has lately shown (Ann. Ch. Pharm. cxxiv. 86) that Laurent's *Azelaic acid* (i. 477) has the same composition as lepargylic or anchoic acid: it appears, however, to differ so much from the latter in melting point, solubility, and the properties of some of its salts, that the two acids can scarcely be regarded as identical (which is Arppe's view), but only as isomeric.

Azelaic acid is most easily obtained by heating castor-oil with 2 pts. of nitric acid, of specific gravity 1·2—1·3, added by small portions, continuing the operation for 12 hours, then separating the acid liquid from the remaining oil, adding fresh acid, and continuing the oxidation for another day. The acid liquid is then to be separated from the oil and added to the former portion, the whole evaporated, with addition of water, and freed from oil, which then separates, by means of a tap-funnel. The clear acid solution duly concentrated yields a white granular mass, which, when freed from oxalic acid by washing with cold and recrystallisation from warm water, and from other more soluble acids by melting the crystals, pulverising the fused mass, and treating the powder with water, leaves a mixture of azelaic and suberic acids; and on treating this residue with cold ether, the azelaic acid is dissolved, while the suberic acid remains behind. The ethereal solution is evaporated, the residue is dissolved in hot water, and the solution, freed from any oil that may still remain, is evaporated to the crystallising point.—Azelaic acid is also obtained in a similar manner, together with several other acids, from almond-oil, spermaceti, and oleic acid (Arppe, Ann. Ch. Pharm. cxx. 288; Jahresber. 1861, p. 357).

Azelaic acid, prepared as above, has the composition $C^9H^{16}O^4$. It crystallises on cooling from a moderately concentrated aqueous solution, sometimes in large laminæ, sometimes in long flattened needles several inches long; the crystals are transparent and colourless, with vitreous lustre, but of no determinate form. From a very dilute solution, it separates in smaller laminæ, which under the microscope exhibit several forms, viz. oblique rhombic prisms with acute angles of about 22°, square tables, and thin flattened prisms. It dissolves in 700 pts. water at 15° (lepargylic or anchoic acid, according to Buckton, in 217·4 pts. at 18°); it is more soluble in ether, and still more in alcohol. It melts at 106° (lepargylic acid at 114—116°, Buckton; partially at 115°, completely at 124°, Wirz); and volatilises with partial decomposition at higher temperatures; the vapours excite coughing, but not so strongly as succinic acid. Heated with caustic baryta, it is resolved into carbonic anhydride and hydride of heptyl, C^7H^{16}, together with small quantities of other hydrocarbons; $C^9H^{16}O^4 = 2CO^2 + C^7H^{16}$. (R. S. Dale, Chem. Soc. J. xvii. 261.)

The azelaates of the alkali- and alkaline-earth-metals are soluble in water, the calcium-salt being the least soluble; those of the heavy metals are insoluble. They are all decomposed by dilute *nitric acid*, with separation of crystalline azelaic acid. The neutral salts form with *chloride of calcium* a copious crystalline precipitate, with *ferric chloride* a brick-red, and with *cupric sulphate* a blue-green precipitate.

Barium-salts.—The *acid salt*, $C^9H^{15}BaO^4$, is obtained by neutralising a hot solution of the acid with carbonate of barium. [Buckton did not succeed in preparing an acid anchoate of barium.]—A warm concentrated solution of the acid neutralised with hydrate of barium yields a granular precipitate of the salt $C^9H^{14}Ba^2O^4.C^9H^{15}BaO^4$, which may be crystallised from water, but when washed with hot water is converted into the *neutral salt*, $C^9H^{14}Ba^2O^4$.

The *calcium-salt*, $C^9H^{14}Ca^2O^4$, is very sparingly soluble. The *copper-salt*, $C^9H^{14}Cu^2O^4$, is a blue-green precipitate; the *lead-salt*, $C^9H^{14}Pb^2O^4$, a white precipitate. The *magnesium-salt*, $C^9H^{14}Mg^2O^4.3H^2O$, is efflorescent, and separates from solution in warm water by evaporation in crystalline crusts. The *manganese-salt*, $C^9H^{14}Mn^2O^4$, is a white fusible precipitate; the *nickel-salt*, an apple-green crystalline precipitate; the *silver-salt*, $C^9H^{14}Ag^2O^4$, a white powder.—The *strontium-salt*, $C^9H^{14}Sr^2O^4.2H^2O$, separates by evaporation from its warm aqueous solution in crystalline crusts, which when dried in the exsiccator, give off half their water, leaving granular crystals containing $C^9H^{14}Sr^2O^4.H^2O$. (Arppe.)

LEPIDINE. $C^{10}H^9N$. (Gr. Williams, Edinb. Phil. Trans. xxi. [3] 377; Gm. xiv. 103.)—A volatile organic base homologous with chinoline, and obtained, together with that base, and several others of the series, by distilling quinine or cinchonine with water and hydrate of potassium (i. 809). The bases are first separated by fractional distillation,—the portion which distils above 199°, especially that between 216° and 243°, consisting of chinoline and lepidine, the latter being found chiefly in the portion boiling above 270°,—and the separation is completed by fractional crystallisation of their platinum-salts.

A base isomeric, and originally supposed to be identical, with lepidine is contained in coal-tar oil, and may be separated by collecting and rectifying the portion which distils between 250° and 267°, and completing the purification by fractional crystallisation of the platinum-salt as above. This base, now called iridoline, is distinguished from lepidine by its lower boiling point, by certain differences in the characters of its salts, some of which crystallise less easily than the corresponding salts of lepidine, and in particular by the reaction of its amyl-derivative with ammonia (p. 573).

Lepidine is an oily base resembling chinoline, of specific gravity 1·072 at 15°, boiling between 266° and 271° (iridoline boils between 252° and 257°). Vapour-density, obs. = 5·14, calc. = 4·96.

Lepidine is somewhat decomposed by boiling, yielding pyrrhol and carbonate of ammonia. By *iodide of methyl*, *ethyl* and *amyl*, it is converted into iodide of methyl-, ethyl- and amyl-lepidyl-ammonium (p. 573).

Both lepidine and iridoline form crystallisable salts; the iridoline-salts smell of naphthalene. The *hydrochlorates* of both bases, $C^{10}H^9N.HCl$, form small colourless needles, which do not melt at 100°. They form, with *chloride of cadmium*, crystalline double salts containing $C^{10}H^9N.HCl.2CdCl$; and with *dichloride of platinum*, the salt $C^{10}H^9N.HCl.PtCl^2$, which is insoluble in alcohol. The platinum-salt of iridoline crystallises less readily than that of lepidine.

The *nitrates*, $C^{10}H^7N.NO^3$, form hard prisms which are permanent in the air, and do not melt at 100°.

Acid chromate of lepidine, $2C^{10}H^9N.H^2O.2Cr^2O^3$, crystallises in long golden-yellow needles which decompose at 100° when moist, but not when dry, and leave chromic oxide when ignited.—*Acid chromate of iridoline* is an oily compound which does not crystallise.

Derivatives of Lepidine.

Amyl-lepidine. $C^{15}H^{19}N = N\left\{\begin{matrix}C^5H^{11}\\ C^{10}H^7\\ H\end{matrix}\right.$.—The hydriodate of this base, or iodide of amyl-lepidyl-ammonium, $C^{15}H^{20}NI = N[(C^5H^{11})(C^{10}H^7)H^2]I$, is obtained by heating lepidine with iodide of amyl, in small crystals, slightly soluble in water. This iodide treated with potash or ammonia is converted into a splendid blue compound (Gr. Williams), called iodide of pelamine; the reaction is,

$$\underset{\substack{\text{Iodide of amyl-}\\ \text{lepidyl-ammonium.}}}{2C^{15}H^{20}NI} + KHO = \underset{\substack{\text{Iodide of}\\ \text{pelamine.}}}{C^{30}H^{39}N^2I} + KI + H^2O.$$

When treated with moist oxide of silver, it yields the base, and from this the other salts of pelamine may be obtained (see PELAMINE). The crude distillate from cinchonine treated with iodide of amyl and potash yields a similar blue compound (known commercially as *chinoline blue* or *cyanine* (i. 873), which consists mainly of iodide of pelamine, together with a small quantity of the homologous compound $C^{28}H^{35}N^2I$, derived in a similar manner from chinoline. (Hofmann, Compt. rend. lv. 849; Proc. Roy. Soc. xii. 410).

Diamyline-lepidine or **Lepamine.** $C^{20}H^{32}N^2 = C^{10}H^{23}N.C^{10}H^9N$, or perhaps $\left.\begin{matrix}(C^5H^{11})^2\\ (C^{10}H^8)''\\ H^2\end{matrix}\right\}N^2$. (Gr. Williams, Chem. Soc. J. xvi. 375.)—When lepidine is cohobated with iodide of amyl, a brown syrupy liquid is obtained, which solidifies to a mass of crystals on cooling. On repeatedly boiling this mass with water, the greater part dissolves, yielding a solution of iodide of amyl-lepidyl-ammonium. A considerable portion however remains undissolved, and this portion, if subjected to prolonged ebullition in a retort with caustic alkalis, decomposes, yielding a distillate consisting of water and an oil. The latter dissolves for the most part in hydrochloric acid, and the solution, evaporated to a moderate bulk, forms two layers, the upper, which appears like a colourless oil, solidifying on cooling to a mass resembling paraffin, while the lower is merely a saturated aqueous solution of the same substance. The paraffin-like hydrochlorate, treated with alkalis and distilled, yields diamyline-lepidine as a volatile base, which may be dried with sticks of potash, and rendered nearly colourless by rectification. It has a fragrant odour, and when perfectly dry distils at about 175°. Vapour-density, obs. = 10·40; calc. = 10·38.

Hydrochlorate of lepamine, $C^{20}H^{32}N^2.2HCl$, melts below 100°, is sparingly soluble in water, and must be dried in a vacuum before being heated over the water-bath.

Chloroplatinate.—On adding an excess of strong hydrochloric acid to a solution of the base, so as to obtain the hydrochlorate as an oil floating on the surface, and then a considerable excess of dichloride of platinum, an adhesive yellow mass is formed, which may be washed by agitation with cold water, dried over oil of vitriol for a day or two and then over the water-bath. It is perfectly soluble in alcohol, and has the composition, $C^{20}H^{32}N^2.2HCl.PtCl^2$.

Gold-salt.—On adding trichloride of gold to a solution of the hydrochlorate, a chocolate-coloured precipitate is formed, which quickly changes to bright green; it is soluble in alcohol, forming a green solution.

Lepamine dissolved in strong *nitric acid* yields a red solution, from which on dilution, a red oil separates, probably a nitro-compound.

By heating lepamine with *iodide of ethyl* in a sealed tube, a syrupy liquid is obtained which when distilled with potash, yields a volatile oily base, probably ethyl-lepamine.

It dissolves readily in hydrochloric acid, forming a salt which is much more difficult to crystallise than hydrochlorate of lepamine.

Ethyl-lepidine. $C^{12}H^{13}N = C^{10}H^8(C^2H^5)N$.—The hydriodate of this base, or *iodide of ethyl-lepidyl-ammonium*, $[(C^2H^5)(C^{10}H^7)H^2]NI$, is obtained by heating lepidine with iodide of ethyl, in brown needles, which after recrystallisation, exhibit a beautiful canary-yellow colour, becoming transiently blood-red at 100°. Treated with moist oxide of silver, it yields the corresponding hydrate, which when treated with hydrochloric acid and dichloride of platinum, yields the platinum-salt, $C^{12}H^{14}NCl.PtCl^2$, soft at first, but soon becoming crystalline.

Methyl-Lepidine, $C^{11}H^{11}N = C^{10}H^8(CH^3)N$.—The hydriodate, or iodide of *methyl-lepidyl-ammonium*, $C^{11}H^{12}NI$, is obtained in crystals by heating lepidine with iodide of methyl.

LEPIDOCROCITE. *Needle Iron ore.*—A hydrated ferric oxide of the same composition as göthite, $Fe^4O^3.H^2O$ (ii. 940), occurring at Spring Mills, Montgomery County, Pennsylvania, in minute radiating crystals or granular scales, and feathery aggregations, imbedded in fibrous red oxide of iron, and in nodules of chalcedony.

LEPIDOLITE. Lithia-mica, found at Rogena and Iglau in Moravia, in the island of Utön, Sweden, and in other localities. (See MICA.)

LEPIDOMELANE. A variety of mica, so called from its scaly structure and black colour (λεπὶs and μέλας), consisting, according to Soltmann's analysis (Pogg. Ann. l. 664) of 37·40 silica, 11·60 alumina, 27·66 ferric oxide, 12·43 ferrous oxide, 9·20 potash, 0·26 lime and magnesia, and 0·60 water, corresponding with the formula $(Fe^2O;K^2O).(Al^4O^3;\ Fe^4O^3).2SiO^2$, which is reducible to that of an orthosilicate, $\left.\begin{matrix}M' \\ (R^2)'''\end{matrix}\right\}SiO^4$.

The mineral forms crude masses of granular scaly structure, consisting of small scales, sometimes exhibiting the form of six-sided tables; according to Wöhler, it is completely decomposed by hot hydrochloric or nitric acid, the silica separating in crystalline scales like those of the mineral. It is found only in one locality in Sweden, probably at Persberg, Wermland.

LEPOLITE. See ANORTHITE (i. 308).

LEPTYNITE. *Granulite* or *Eurite.* A granular compound of felspar with quartz, sometimes containing garnet.

LEUCANILINE. $C^{20}H^{21}N^3$. (A. W. Hofmann, Proc. Roy. Soc. xii. 2; Jahresber. 1862, p. 34.)—A base produced by the action of reducing agents on rosaniline, and related to it in the same manner as indigo-white to indigo-blue:

$$\underset{\text{Rosaniline.}}{C^{20}H^{19}N^3} \quad + \quad H^2 \quad = \quad \underset{\text{Leucaniline.}}{C^{20}H^{21}N^3}.$$

It may be obtained by leaving hydrochlorate of rosaniline in contact with metallic zinc, or more easily by digesting a salt of rosaniline (or commercial fuchsine or magenta) with sulphide of ammonium. A yellow resinous mass is then formed, which is to be finely pulverised, washed with water and dissolved in dilute hydrochloric acid. The solution forms with concentrated hydrochloric acid, a copious, crystalline, brown or yellow precipitate, of impure hydrochlorate of leucaniline, which may be purified by repeated solution in dilute, and precipitation by concentrated hydrochloric acid. It crystallises from boiling dilute hydrochloric acid in very small rectangular plates, which are obtained quite pure by recrystallisation from water, or by precipitation of the alcoholic solution with ether.

Leucaniline is precipitated from the solution of the hydrochlorate as a white powder, acquiring a faint rose tint on exposure to the air. It is nearly insoluble in cold, sparingly soluble in boiling *water*, whence it separates in small crystals, slightly soluble in *ether*, easily in *alcohol*. It turns red when heated, and melts at 100° to a dark-red transparent liquid, which solidifies to a lighter-coloured mass on cooling. By oxidising agents, such as peroxide of barium, ferric chloride, and especially chromate of potassium, it is easily converted into rosaniline. It unites with sulphide of carbon, chloride of benzoyl, and several other bodies, forming compounds which have not yet been examined.

The salts of leucaniline crystallise well, especially the sulphate; they are all soluble in water, and are precipitated by acids. The *hydrochlorate*, $C^{20}H^{21}N^3.3HCl.H^2O$, gives up its water only when heated for a long time in a stream of hydrogen. On boiling its solution with excess of leucaniline, the latter separates out in splendid crystals, without forming a less acid salt. The *chloroplatinate*, $C^{20}H^{21}N^3.3HCl.3PtCl^2.H^2O$, is sparingly soluble in cold water, decomposible by boiling water, and gives up its water with difficulty, even when heated above 100°. The *nitrate*, $C^{20}H^{21}N^3.3HNO^3.H^2O$, forms white needles soluble in water and in alcohol, but not in ether, only sparingly in nitric acid, and decomposing at 100°.

Triphenyl-leucaniline. $C^{20}H^{18}(C^6H^5)^3N^3$.—Obtained by the action of reducing agents on triphenyl-rosaniline. The blue solution of the hydrochlorate of this base is decolorised by zinc and hydrochloric acid, and the clear liquid treated with water yields a precipitate which may be purified by solution in ether. The same compound is obtained as a brittle, non-basic resin, by the action of sulphide of ammonium on hydrochlorate of triphenyl-rosaniline. It is anhydrous, and when treated with oxidising agents, is reconverted into triphenyl-rosaniline. (Hofmann, Compt. rend. lvii. 25.)

LEUCAZOLITMIN. See LITMUS.

LEUCHTENBERGITE. A variety of chlorite (i. 914) from Slatoust in the Ural. Breithaupt regards it as an altered chlorite. Komonen found in it only 8·62 per cent. water instead of 12·62, the percentage in normal chlorite. Kenngott regards it as a distinct species.

LEUCIC ACID. $C^6H^{12}O^3$. (Strecker, Ann. Ch. Pharm. lxviii. 55; Gössman, *ibid.* xci. 135; Waage, *ibid.* cxviii. 295; Thudichum, Chem. Soc. Qu. J. p. xiv. 307; Frankland, Proc. Roy. Soc. xii. 396; Frankland and Duppa, *ibid.* xiii. 140.)—An acid, homologous with lactic acid, produced:—1. From *leucine.*—*a.* When nitric oxide gas is passed through a solution of leucine in strong nitric acid, nitrogen is evolved and leucic acid is formed (Strecker). The same reaction takes place when nitrous acid is passed through a solution of leucine in warm water (Thudichum), or water slightly acidulated with nitric acid (Waage):

$$\underset{\text{Leucine.}}{C^6H^{13}NO^2} + \underset{\text{Nitrous acid.}}{HNO^2} = \underset{\text{Leucic acid.}}{C^6H^{12}O^3} + N^2 + H^2O.$$

Cahours had previously observed (Compt. rend. xxvii. 368) that a peculiar acid is formed when an aqueous solution of leucine is left to itself.—*β.* When chlorine gas not in excess is cautiously passed through a solution of leucine in caustic soda, leucic acid is formed and may be separated from the mixture in the same manner as benzoglycollic acid (i. 548) from hippuric acid. (Gössmann.)

2. From *oxalate of ethyl*, by the action of zinc-ethyl. The direct product of this action is probably zincoleucic ether, a body not isolated, thus:

$$\underset{\text{Oxalate of ethyl.}}{C^6H^{10}O^4} + \underset{\text{Zinc-ethyl.}}{\left\{\begin{matrix}ZnC^2H^5\\ZnC^2H^5\end{matrix}\right.} = \underset{\text{Zincoleucic ether.}}{C^6H^{10}(ZnC^2H^5)O^3} + \underset{\text{Ethylate of zinc.}}{Zn(C^2H^5)O.}$$

The zincoleucic ether is converted by the action of water into leucic ether:

$$\underset{\text{Zincoleucic ether.}}{C^6H^{10}Zn(C^2H^5)O^3} + H^2O = \underset{\text{Leucic ether.}}{C^6H^{11}(C^2H^5)O^3} + ZnHO;$$

and from this, the barium-salt, and thence the acid itself, is easily obtained. (Frankland.)

Preparation.—1. Pure leucine is dissolved in boiling water slightly acidulated with nitric acid; nitrous acid gas is passed through the warm solution as long as nitrogen continues to escape; the liquid, which turns brown and gradually deposits brown flakes, is left to cool, then agitated several times with ether; and the ethereal extracts are evaporated. The residue is a brown oily liquid not miscible with water, which gradually solidifies to a radio-crystalline mass. The aqueous solution, freed from leucic acid by repeated agitation with ether, left on evaporation a considerable quantity of nitro-leucic acid.—To purify the crude leucic acid thus obtained, it is dissolved in a large quantity of water (a smaller quantity dissolves it but imperfectly); the boiling liquid is mixed with an aqueous solution of acetate of zinc; and the precipitated leucate of zinc is washed on the filter with water (which dissolves but a small quantity of it), purified by recrystallisation from alcohol, then suspended in water, and decomposed by sulphuretted hydrogen. The filtered solution is but very slightly coloured, and when evaporated to a syrup and left to stand, yields leucic acid in colourless needles. If, on the other hand, the zinc-salt be suspended in alcohol and decomposed by sulphuretted hydrogen, the acid is obtained in hard, brittle prisms. (Waage.)

2. Thudichum passes nitrous acid gas through a warm aqueous solution of leucine; evaporates, with addition of leucine, to neutralise the free nitric acid, and prevent it from oxidising the leucic acid; agitates the syrupy residue with ether (or extracts the leucic acid from the aqueous solution by agitation with ether, without previous evaporation; in which case, however, the treatment with ether must be repeated a great number of times)—and purifies the crude leucic acid from adhering brown oil, either by solution in cold water, filtration and recrystallisation,—or by strongly pressing the coloured crystals between bibulous paper—or by precipitating the aqueous solution

with acetate of lead, decomposing the washed precipitate with sulphuretted hydrogen, and evaporating the filtrate either over the water-bath at a very moderate heat, or over sulphuric acid.

3. Oxalic ether is mixed with its own weight of zinc-ethyl, in a vessel surrounded by cold water, to prevent rise of temperature and the consequent occurrence of a secondary reaction, attended with the evolution of large quantities of ethylene and hydride of ethyl; towards the end, however, the reaction requires to be assisted by the application of a gentle heat. The mixture, which generally remains fluid, is mixed after cooling, with its own volume of water (whereupon torrents of hydride of ethyl, derived from excess of zinc-ethyl, are evolved), and subsequently distilled in a water-bath. Weak alcohol containing an ethereal oil in solution then passes over, and a further quantity of the oil may be obtained by adding water to the residue in the retort, and continuing the distillation on a sand-bath. The oil is precipitated from the alcoholic distillate by water, added to that which floats on the surface of the watery distillate, then dried over chloride of calcium, and rectified. The principal portion, which distils between 174° and 176°, consists of leucic ether. (Frankland.)

The process may be greatly simplified, and a larger product obtained, by generating the zinc-ethyl during the reaction, namely by heating a mixture of amalgamated zinc, iodide of ethyl, and oxalic ether to the necessary temperature. The operation may be considered complete when the mixture has solidified to a resinous-looking mass; and this, when treated with water as above, and distilled, yields a considerable quantity of leucic ether. (Frankland and Duppa.)

The leucic ether heated with hydrate of barium, is converted into leucate of barium, and this when decomposed by dilute sulphuric acid, yields a solution of leucic acid.

Properties.—Leucic acid forms colourless needles (Strecker); needles or hard, brittle prisms, of the trimetric or monoclinic system, according to the mode of preparation (Waage); radiary group of needles, having a mother-of-pearl lustre, with a beautiful variety of concentric markings, like those of some kinds of larch-agaric (Thudichum); it is heavier than water, and cuts like hard soap, almost like stearic acid (Thudichum); it has an acid taste, and reddens litmus (Thudichum); a bitter taste, and strong acid reaction (Waage). It melts below 100° and solidifies on cooling (Thudichum); melts at 73°, and sometimes solidifies at a few degrees below the melting point, sometimes remains liquid even when cooled to 0° (Waage). It is easily soluble in *water* and in *alcohol*, soluble also in *ether*.

Decompositions.—1. Leucic acid volatilises at 100°, apparently without decomposition. When it is placed on a watch-glass and heated over the water-bath, the sides of the glass become fringed with crystals of the sublimed acid, which dissolve easily in water, leaving, however, a few flocks, probably consisting of the anhydride. The mass which remains in the middle of the watch-glass is syrupy, dissolves in water only after prolonged boiling, but is easily soluble in alcohol and ether; it probably also consists of leucic anhydride (Waage). The acid heated for some time in the water-oven, continually gives off acid-smelling vapours, and does not afterwards solidify on cooling, but remains in the form of an uncrystallisable, dark-brown, smeary syrup; the anhydride, which has a very disagreeable odour, remains unchanged, even when left over oil of vitriol for weeks, and is nearly insoluble in water, separating from it like an oil and sinking to the bottom. A small quantity of this insoluble compound is likewise formed, when the aqueous solution, even if dilute, is heated to the boiling point or evaporated (Thudichum). Leucic acid may be boiled with water without decomposition, and traces only of it distil off with the water (Frankland).—2. Leucic acid strongly heated in the *air*, gives off thick fumes and blackens, then takes fire and burns with a yellow smoky flame, leaving a small quantity of charcoal, which is quickly and easily consumed. (Thudichum.)

Leucates. Leucic acid forms crystallisable salts, the composition of most of which may be represented by the formula, $C^6H^{11}MO^3$. An acid silver-salt appears however, to exist, which is perhaps $C^6H^{11}AgO^3.C^6H^{12}O^3$. But according to the larger atomic weights now assigned to most of the metals, the formula of the acid should be $C^{12}H^{24}O^6$, and that of its normal salts, $C^{12}H^{22}M''O^6$. The acid silver-salt will then be $C^{12}H^{23}AgO^6$. The salts are for the most part obtained by boiling the aqueous solution of the acid with the corresponding carbonates (Thudichum). They are less soluble than the lactates in water, more soluble in alcohol. (Waage.)

Leucate of Ammonium.—The acid slightly supersaturated with ammonia, and evaporated, leaves a thick homogeneous residue, in which no trace of crystallisation can be observed, even after drying for several weeks over oil of vitriol. (Thudichum.)

Leucate of Barium, $C^6H^{11}BaO^3$ or $C^{12}H^{22}BbaO^6$.—Obtained by digesting the aqueous acid with carbonate of barium, or by heating leucic ether with hydrate of barium, separating the excess of baryta by carbonic acid, filtering and evaporating

(Frankland, Waage, Thudichum). It dissolves with moderate facility in warm water and dilute alcohol, and separates from boiling alcohol in beautiful colourless, silky, laminar crystals, which, like most leucates, retain something of the appearance of leucine. (Waage.)

Leucate of Calcium, $C^6H^{11}CaO^3$ or $C^{12}H^{22}CcaO^6$.—An aqueous solution of the acid neutralised with chalk or milk of lime, and left to evaporate, yields the calcium-salt in fine needles, easily soluble in water and in alcohol.

Leucate of Cobalt, $C^6H^{11}CoO^3$ or $C^{12}H^{22}CcoO^6$.—The dilute aqueous acid boiled with excess of carbonate of cobalt, then filtered and evaporated, deposits light crusts of a pink colour while moist, but of a very pale rose-colour or almost white when dry. The salt is but sparingly soluble in cold water, and not much more soluble at the boiling heat. It crystallises in needles, which, under the microscope, appear to be arranged in globular masses. (Thudichum.)

Leucate of Copper.—When a dilute aqueous solution of leucic acid is treated with a dilute solution of ammonio-sulphate of copper, the colour of the copper-salt changes to light-green. On boiling the liquid, it becomes paler, and on cooling deposits light green granules of leucate of copper. Under high powers of the microscope, these granules appear as balls, formed by a radiary arrangement of needles (Thudichum). A solution of leucic acid mixed with acetate of copper, forms a green flocculent precipitate, very sparingly soluble in water, even at the boiling heat, but easily crystallised from boiling alcohol, from which it separates in very beautiful light blue, shining, bulky scales, which do not undergo any diminution in weight at 100°. (Waage.)

Leucate of Lead.—On adding acetate of lead to a solution of leucic acid or a leucate, a copious white flaky precipitate is formed, which on boiling dissolves almost entirely in the liquid. Any portion remaining undissolved melts into a white mass, which is soft like resin while warm, but becomes brittle and hard on cooling. This substance is insoluble in water and alcohol, even on boiling, and seems to be a basic salt.

If the solution of lead is added to a boiling solution of the acid, no precipitate ensues, acid vapours are evolved, and the liquid becomes milky on cooling. In a short time, it deposits the lead-salt as a light, granular, white mass, which, under the microscope, appears to be made up of a multitude of strongly refracting spherical masses, of the size of human blood-corpuscles. This salt is more easily soluble in an excess of the acetate than in water. It is easily soluble in spirit of wine, particularly in boiling spirit. Even in these solutions, basic salts are easily formed. The addition of water to these solutions produces a precipitate. (Thudichum.)

Leucate of Magnesium.—Sparingly soluble in water, deposited in crusts on evaporation. (Thudichum.)

Leucates of Mercury.—*Mercuric Leucate* may be prepared:—*a*. Directly, by dissolving freshly-precipitated moist mercuric oxide in aqueous leucic acid. A flaky precipitate gradually ensues, which on heating becomes red and granular, and adheres to the sides of the glass. On cooling, a new precipitate, consisting of whitish globules, is deposited.—*b*. By adding mercuric nitrate to an aqueous solution of leucic acid, a whitish-red precipitate is formed, which dissolves on boiling, and on cooling is again deposited in reddish granules.—*c*. By adding the mercurial solution to the leucate of an alkali-metal.

Mercurous Leucate.—When a solution of mercurous nitrate is added to a solution of leucic acid a slight turbidity ensues. The addition of carbonate of sodium produces a copious reddish-white precipitate, which, on boiling, becomes red, then dull grey, and deposits metallic mercury. (Thudichum.)

The leucates of mercury have a great tendency to become reduced. The mercuric salt easily passes into the mercurous salt. The mercuric salt, moreover, has a great tendency to become basic and insoluble. (Thudichum.)

Leucate of Potassium is produced by the action of aqueous potash on leucic ether, and separates as a semi-solid soap on the surface of the potash-solution, if the latter is concentrated. (Frankland.)

Leucates of Silver.—*a*. *Neutral-salt*, $C^6H^{11}AgO^3$ or $C^{12}H^{22}Ag^2O^6$, is obtained by adding nitrate of silver to the solution of the acid neutralised with ammonia, or by boiling the acid with oxide of silver, and may be rendered quite colourless by recrystallisation from boiling water, in which it is moderately soluble. It is anhydrous (Waage). Nitrate of silver added to a warm solution of leucate of ammonium, potassium, or sodium, forms a copious white crystalline precipitate, which increases as the liquid cools, and blackens if left in the mother-liquor (Thudichum). It contains 45·2 per cent. silver (Waage); 44·14 (Thudichum); calc. 45·19 per cent.

Acid salt, $C^{12}H^{23}AgO^6$.—A hot dilute solution of leucic acid decomposes recently precipitated carbonate of silver, with effervescence. The excess of the carbonate of silver and the undissolved portion of the leucate become blackish-grey, but the acid is not entirely neutralised. The hot filtrate forms no deposit on cooling. The attempt to evaporate it over the water-bath produces a black precipitate of reduced silver. It must, therefore, be evaporated in vacuo over oil of vitriol. After prolonged standing, a few crystals, of a glassy lustre and appearing under the microscope as groups of rhombic plates, are deposited at the margin of the dish. The liquid then becomes covered with a pellicle, and evaporation is impeded. At a later stage conglomerates of needles are deposited, which, when carefully dried over sulphuric acid in vacuo, appeared a little blackened, like most silver-salts, but are not decomposed. Silver by analysis 26·97 per cent.; the formula requires 29·1 per cent. (Thudichum.)

Leucate of Sodium.—The aqueous acid neutralised with carbonate of sodium, and evaporated, leaves a syrupy residue covered with a crystalline crust. When this syrup is left over oil of vitriol, crystals form in it, which under the microscope exhibit a characteristic tub-shape, with rhombic plates interspersed here and there. (Thudichum.)

Leucate of Zinc, $C^6H^{11}ZnO^3$ or $C^{12}H^{22}ZnO^6$.—This salt is obtained by neutralising the dilute acid at the boiling heat with carbonate of zinc, and filtering at the same temperature. The solution deposits a thin crust on cooling. Evaporated over the water-bath, it soon becomes covered with a crust, and on cooling deposits bulky masses of needles, which must be separated by filtration, pressed between bibulous paper, and dried by exposure to the air or over the water-bath. The best crystals are obtained from a solution containing excess of leucic acid (Thudichum). For Waage's mode of preparation, see page 575.

The salt is snow-white, with splendid silky lustre; exhibits under the microscope the appearance of masses of needles (Thudichum); extremely light scales, of dazzling whiteness and silky lustre (Waage). It is sparingly soluble even in boiling water, less in cold water (Thudichum); dissolves in 300 pts. water at 16°, and in 204 pts. boiling water, more soluble in alcohol (Waage). The air-dried salt contains $2C^6H^{11}ZnO^3.H^2O$ or $C^{12}H^{22}ZnO^6.H^2O$, and gives off its water (5·1 per cent.) at 100° (Waage). The anhydrous salt gives by analysis, 43·87 per cent. carbon, 6·39 hydrogen, and 20·10 zinc, the formula requiring 44·01 carbon, 6·72 hydrogen, and 19·92 zinc (Thudichum). Sulphydric acid precipitates the zinc completely (Waage); according to Thudichum, on the contrary, the precipitation is only partial, even after the solution has been repeatedly saturated with the gas.

LEUCIC ETHER. *Leucate of Ethyl,* $C^8H^{16}O^3 = C^6H^{11}(C^2H^5)O^3$.—The formation and preparation of this compound by the action of zinc-ethyl on oxalic ether have already been described (p. 575). It is a colourless, transparent, somewhat oily liquid, possessing a peculiar penetrating ethereal odour, and a sharp taste. It is insoluble in water, but dissolves readily in alcohol and ether. Specific gravity 0·9613 at 18·7°. Boiling point, 175°. Vapour-density, obs. = 5·241; calc. 5·528. Treated with hydrate of barium or potassium, it yields the corresponding salts of leucic acid. (Frankland.)

LEUCINDIN-SULPHURIC ACID. See INDIN-SULPHURIC ACID (p. 268).

LEUCINE. $C^6H^{13}NO^2$. Formerly called *Aposepedine* and *Caseous Oxide.* (Proust, Ann. Ch. Phys. [2] x. 40; Braconnot, *ibid.* xiii. 119; Mulder, J. pr. Chem. xvi. 290; Bopp, Ann. Ch. Pharm. lxix. 20; Laurent and Gerhardt, Ann. Ch. Phys. [3] xxiv. 321; Cahours, Compt. rend. xxvii. 265; Limpricht, Ann. Ch. Pharm. xciv. 243; Gössmann, *ibid.* xc. 184; xci. 129; Strecker, *ibid.* lxviii. 54; Gm. xi. 426.) —This substance was first observed by Proust, in 1818, as a product of the putrefaction of cheese; and Braconnot in 1820 found it among the products of decomposition of animal substances by sulphuric acid; Mulder, in 1838, showed that the two substances thus obtained were identical.

It is homologous with glycocine ($C^2H^5NO^2$) and alanine ($C^3H^7NO^2$), and may be regarded as lactamic acid, $\left.\begin{array}{c} H^2 \\ (C^6H^{10}O)'' \\ H \end{array}\begin{array}{l} \}N \\ \\ \}O \end{array}\right.$, being related to leucic acid in the same manner as glycocine to glycollic acid, and alanine to lactic acid.

Occurrence.—In old cheese (Proust). In fresh calf's liver (Liebig, Chem. Briefe, 3 Aufl. 453); also, together with tyrosine, in the human liver, in certain cases of disease, but not in the healthy liver (Frerichs and Städeler, Jahresber. 1854, p. 675). According to later researches by these chemists (*ibid.* 1856, 702; 1858, 550), leucine and tyrosine are very widely diffused in the animal organism. Leucine also exists, together with taurine, inosite, and uric acid, in the tissue of the lungs (A. Cloëtta, Ann. Ch. Pharm. xcii. 289). According to Gorup-Besanez, Ann. Ch. Pharm. xcviii. 7), it occurs in many parts of the glandular system, viz., in the thymoïd and thyroïd glands, in the liver, and especially in the pancreas. It has been found also in the brain of oxen (**W. Müller**, Ann. Ch. Pharm. ciii. 131); in the pancreas of oxen (**Scherer**, Jahresber. 1859, p. 610); in the stomach and intestines of the pupæ of butterflies (**Schwarzenbach**, *ibid.* 1857, p. 538), and in the fly-agaric, *Agaricus muscarius.* (**Ludwig**, *ibid.* 1862. p. 516.)

Formation.—1. In the decomposition of gelatin, muscular flesh, legumin or wool (or white of egg, according to Mulder), by sulphuric acid (**Braconnot**); together with a small quantity of glycocine (**Mulder**). **Gorup-Besanez** also (Ann. Ch. Pharm. cxviii. 230), by treating wool with sulphuric acid, obtained, together with volatile acids and a large quantity of ammonia, about 3 per cent. of tyrosine, and a rather large quantity of leucine containing sulphur. The leucine was obtained free from sulphur by dissolving it in rather dilute potash-ley, boiling it with a solution of lead-oxide in potash, filtering from sulphide of lead, neutralising the filtrate with sulphuric acid, evaporating to dryness, boiling the pulverised residue with alcohol, and leaving the solution to crystallise.

2. By heating horn with dilute sulphuric acid (**Hinterberger**), also together with tyrosine, by heating elastic tissue, especially the cervical ligament (**Zollikofer**), or feathers, hedge-hogs' spines, human hair, the wing-cases of cockchafers, or globulin and hæmatin from ox-blood (**Leyer** and **Köller**, Ann. Ch. Pharm. lxxxiii. 332), or silk (**Hinterberger**, Wien. Akad. Ber. xi. 450) or conchiolin (**Schlossberger**, Zeitschr. Ch. Pharm. 1860, p. 424), with dilute sulphuric acid. **Erlenmeyer** and **Schöffer** (Zeitschr. Ch. Pharm. 1859, p. 315), by boiling 1 pt. of various albuminous and gelatinous substances with 5 pts. of a mixture of 1 pt. sulphuric acid (H^2SO^4) and 1½ pts. water, obtained the following quantities of leucine and tyrosine: Cervical ligament yielded ¼ per cent. tyrosine and 38 to 45 per cent. leucine; blood-fibrin, 2 per cent. tyrosine (on evaporating the neutral liquid to about 1·08 to 1·10 specific gravity), then 14 per cent. leucine; flesh-fibrin, not quite 1 per cent. tyrosine, and about 18 per cent. leucine; white of hen's egg, 1 per cent. tyrosine and about 10 per cent. leucine; horn (treated with 10 pts. of the above acid mixture), 3·6 per cent. tyrosine, and about 10 per cent. leucine. The several substances were decomposed by three hours' boiling with the acid as completely as when the boiling was continued for 36 or 40 hours.

3. By the action of dilute acids upon indican. (**Schunck**, p. 247.)

4. By boiling white of egg, gelatin, or flesh, with potash-ley, glycocine being formed at the same time (**Mulder**). Hence also, when the juice of mangold-wurzel is boiled with lime. (**Hochstetter**, J. pr. Chem. xxix. 36.)

5. By melting albumin, fibrin, casein (**Bopp**), or horn (**Hinterberger**) with hydrate of potassium.

6. In the putrefaction of casein or gluten under water (**Proust**, **Mulder**); sometimes abundantly, sometimes only in traces (**Cahours**). Also, together with tyrosine, ammonia, butyric acid, and lactic acid, by the putrefaction of yeast (**A. Müller**, J. pr. Chem. lvii. 162, 447). But according to **Hesse** (J. pr. Chem. lxx. 34), the substance regarded by **Müller** as leucine contains 3 or 4 per cent. sulphur, and is more soluble in alcohol than leucine (see PSEUDOLEUCINE, p. 582).

7. By the action of hydrocyanic acid and dilute hydrochloric acid, with the aid of heat, on valeral-ammonia (**Parkinson**, Ann. Ch. Pharm. xc. 144; **Limpricht**, *ibid.* xciv. 243):

$$NH^3.C^5H^{10}O + CNH + HCl + H^2O = C^6H^{13}NO^2 + NH^4Cl.$$

It was stated by Gössmann, that thialdine is converted into leucine by the action of moist silver-oxide, according to the equation:

$$C^6H^{13}NS^2 + 2Ag^2O = C^6H^{13}NO^2 + 2Ag^2S;$$

but according to **Hofmann** (Chem. Soc. J. x. 193), thialdine thus treated gives off the whole of its nitrogen in the form of ammonia.

Preparation.—1. Finely-chopped beef, washed with water and then strongly pressed, is mixed with an equal weight of oil of vitriol, and gently heated till it is completely dissolved; the fat is skimmed off after cooling; the mixture diluted with water amounting to 3½ times the weight of the meat; the liquid boiled for 9 hours, with frequent renewal of the water; the sulphuric acid removed by chalk; the filtrate evaporated to an extract; this extract repeatedly boiled with alcohol of 34° Bm.; the resulting alcoholic tincture evaporated; the dry residue exhausted with cold alcohol; the residual mixture of leucine and a small quantity of matter precipitable by tannin dissolved in water; a solution of tannin carefully added to it by drops as long as any precipitate ensues; and the liquid filtered after a few seconds, then evaporated (**Braconnot**). The leucine prepared by Braconnot appears still to have contained glycocine. (**Mulder.**)

2. 1 pt. of dry albumin, fibrin, or casein, free from fat, is boiled with 4 pts. of oil of vitriol and 12 pts. of water, in an open vessel, the ebullition being continued for a day

and the water continually renewed. Or, better: 1 pt. of the substance is dissolved in 4 pts. of strong hydrochloric acid; the liquid mixed with 3 or 4 pts. of oil of vitriol and evaporated over the water-bath till the greater part of the hydrochloric acid is expelled, and the remaining black-brown pitchy or syrupy mass, in which minute crystals form, is dissolved in hot water. Either of these acid liquids is boiled with excess of milk of lime to expel ammonia, then strained through a linen bag; the clear filtrate treated with sulphuric acid to precipitate the lime which is held in a solution by a product of decomposition; the excess of acid precipitated by acetate of lead, and the excess of lead by sulphydric acid; and the filtrate evaporated to a syrup, from which in a few days leucine and tyrosine crystallise. The crystals are freed from the syrupy mother-liquor by digestion in 86 per cent. alcohol, and the leucine separated from the tyrosine and brown matter by treatment with water, hydrated oxide of lead, and animal charcoal, as in the fifth mode of preparation.

3. 1 pt. of cow-horn shavings is boiled with 4 pts. of oil of vitriol and 12 pts. of water for 36 hours, the water being renewed from time to time, the liquid then supersaturated with milk of lime; the whole boiled for 24 hours in an iron pot, then strained through a conical bag and squeezed, and the liquid mixed with a very slight excess of sulphuric acid, filtered, and evaporated; it then yields at first spherical crystalline masses of tyrosine, and afterwards laminated masses of leucine. The latter are pressed between paper, freed from brown matter by washing with absolute alcohol, and crystallised from solution in a small quantity of hot water, tyrosine then separating first, and the mother-liquor afterwards yielding leucine, tolerably pure but not quite white. It must therefore be dissolved in hot water; digested with a small quantity of hydrated oxide of lead; the liquid filtered; the filtrate freed from lead by sulphydric acid, and the crystallised leucine further treated with animal charcoal (Hinterberger, Ann. Ch. Pharm. lxxi. 72). H. Schwanert (*ibid.* cii. 221) boils 2 lbs. of horn-shavings with 5 lbs. sulphuric acid and 13 lbs. water for 24 hours, renewing the water as it evaporates, then supersaturates with lime, and, after filtering off the gypsum, evaporates the filtrate to 12 lbs. and mixes it with a quantity of oxalic acid sufficient to produce a slight acid reaction. The liquid filtered from calcic oxalate, and evaporated till a crystalline film forms upon its surface, deposits groups of yellowish laminæ of leucine mixed with tyrosine, more of which crystals may be obtained by evaporating the mother-liquor. The crystalline mass is then dissolved in such a quantity of hot water that the solution on cooling yields crystals of tyrosine only; the leucine solution is then decolorised with animal charcoal, evaporated, and the leucine which separates is purified by pressure and recrystallisation from hot alcohol. Waage (Ann. Ch. Pharm. cxviii. 295) proceeds in the same way as Schwanert, excepting that, after precipitating the last portions of lime with oxalic acid, he mixes the filtrate with sulphate of copper, precipitates the copper with sulphydric acid; evaporates the filtered liquid which is then nearly colourless, to the crystallising point; recrystallises the separated leucine from water and dilute alcohol; and finally decolorises it by boiling with a small quantity of hydrate of lead, and removing the lead by sulphydric acid. The leucine thus prepared still retains 2 per cent. ash and a trace of sulphur.

4. White of egg, gelatin, or flesh, is boiled with potash-ley till it is completely decomposed; the liquid neutralised with sulphuric acid, and evaporated; and the leucine extracted with alcohol. (Mulder.)

5. 1 pt. of the powder of dry albumin, fibrin, or casein free from fat, is added to 1 pt. of hydrate of potassium, heated to fusion in an iron crucible of 25 times the capacity; and water carefully added after half an hour, when the violent frothing arising from the escape of water and ammonia has subsided, and the brown colour which the mixture at first exhibits, is changed to yellow; if the liquid be then saturated with acetic acid, filtered hot, and gradually cooled, it yields tufts of needles consisting of tyrosine. These crystals completely fill the filtrate, when the process is well conducted; on the other hand, they are less abundant the longer the fusion has been continued.—The liquid decanted from the crystals of tyrosine is evaporated till a crystalline film appears on the surface; then set aside for 24 hours and exhausted with strong alcohol, which leaves crystals of leucine and the still remaining tyrosine; the liquid is mixed with alcoholic sulphuric acid, and decanted from the crystallised sulphate of potassium; the alcohol separated from it by evaporation, the sulphuric acid by lead, and then the lead by sulphydric acid; and the solution finally evaporated, whereupon it yields crystals of leucine and a greasy syrup, the quantity of which is less in proportion as the fusion has been longer continued. To purify the leucine from tyrosine and a small quantity of brown colouring matter, it is dissolved in such a quantity of hot water that only a small quantity of leucine may separate on cooling, together with the tyrosine; the mother-liquor is digested with hydrated oxide of lead, which removes the colouring matter together with a small quantity of leucine; the filtrate is treated with sulphydric acid; and the filtrate thus obtained, which has merely a yellowish colour, is evaporated in a flask till a crystalline film forms on its surface. It then, on cooling, yields crystals

of leucine, which must be washed with cold water and alcohol, and decolorised by treatment with animal charcoal and recrystallisation.—If the object be merely to obtain leucine, and not tyrosine, it is sufficient to heat the potash-mixture till the strongest intumescence is over. At that stage of the process, the same quantity of leucine is formed, but no tyrosine. (**Bopp.**)

6. One pt. of cheese, muscular flesh, or white of egg, is left to putrefy with 50 pts. of water for six weeks at a temperature somewhat above 20°; the resulting turbid solution boiled with a small quantity of milk of lime; the lime precipitated by a very slight excess of sulphuric acid; the filtrate boiled down and precipitated by neutral acetate of lead; the decanted liquid treated with sulphydric acid; the filtrate evaporated to a syrup; and the leucine which crystallises therefrom, is freed from the remaining syrup by means of alcohol, and purified by solution in water, treatment with hydrated oxide of lead and sulphydric acid, crystallisation, and washing with cold water and alcohol. When the above-mentioned alcoholic solution of the syrup is evaporated to complete dryness, and the residue dissolved in absolute alcohol, the solution still deposits a small quantity of leucine. (**Bopp.**)

7. The cervical ligament of the ox, after being freed from the surrounding fibrous tissue by boiling with water containing acetic acid, and subsequent scraping with a knife, and (if necessary) from fat by digestion in ether, is boiled for 48 or 50 hours with dilute sulphuric acid (8 pts. oil of vitriol to 12 pts. water), the water being replaced as it evaporates. The resulting solution is mixed with a slight excess of thin milk of lime, and boiled for some hours; the filtrate exactly neutralised with sulphuric acid and evaporated; and the liquid, after filtration from the separated sulphate of calcium, is again evaporated: it then yields, especially on cooling, impure leucine, which may be purified by recrystallisation from hot alcohol. This process is peculiarly advantageous, as the acid mother-liquors crystallise to the last drop, yielding nothing but leucine. (**Zollikofer**, Ann. Ch. Pharm. lxxxii. 162; compare **Gössmann**, *ibid.* xci. 130.)

8. Valeral-ammonia is boiled in a retort with hydrocyanic and hydrochloric acids till the oily layer consisting of the fused ammonia-compound has completely disappeared; the solution is then left to itself till the greater part of the resulting chloride of ammonium has crystallised out; the hydrochloric acid removed by means of hydrated oxide of lead, and the lead by sulphydric acid; the filtrate is evaporated over the water-bath, and the residue dissolved in hot dilute alcohol: the solution thus obtained yields crystals of pure leucine. (**Limpricht.**)

Properties.—Leucine crystallises from alcohol in soft nacreous scales, lighter than water and resembling cholesterin. It sublimes completely at 170°, in cotton-like flocks without fusion or decomposition (**Mulder**); according to **Schwanert**, on the contrary, it melts at 170°. It is sparingly soluble in cold, but dissolves easily in hot *water*; sparingly in alcohol of ordinary strength (in 658 pts. of cold alcohol of specific gravity 0·828 according to **Mulder**), very sparingly in absolute alcohol. According to **Zollikofer**, it dissolves in about 27 pts. of cold water, in 1040 pts. of cold alcohol of 96 per cent., and in 800 pts. hot alcohol of 98 per cent. It is insoluble in ether. Its solubility in water and alcohol is increased by the presence of acetic acid, or an alkaline acetate.

Decompositions.—1. Leucine heated to 180°, yields a yellow distillate having an ammoniacal odour, and solidifying in the cold, while a brown resinous mass remains in the retort. The alcoholic solution of the distillate has an alkaline reaction, and when treated with hydrochloric acid, gives off carbonic anhydride, and yields a solution containing hydrochlorate of amylamine, together with sal-ammoniac. The resolution of the leucine into carbonic anhydride and amylamine, which is the principal reaction, is similar to that of phenyl-carbamic acid into carbonic anhydride and phenylamine, and shows that leucine may be regarded as amyl-carbamic acid:

$$\underset{\text{Leucine.}}{C^6H^{13}NO^2} = CO^2 + \underset{\text{Amylamine.}}{C^5H^{13}N}. \quad \text{(Schwanert.)}$$

—2. Leucine heated in contact with the air burns readily, and with a white flame. —3. An alkaline solution of leucine exposed to the action of *ozone*, yields carbonic acid, butyric acid, and other volatile fatty acids, ammonia, and probably also, in the earlier stage of the decomposition, cyanic acid and valeraldehyde (**Gorup-Besanez**, Ann. Ch. Pharm. cxxv. 210).—4. Leucine is decomposed by *chlorine*, forming a hard brown body, similar to that obtained with glycocine (ii. 903), and a red volatile liquid (**Mulder**). When chlorine is passed into water in which leucine is suspended, carbonic anhydride is evolved, and a turbid solution is formed, from which an oily liquid separates, consisting of a mixture of valeronitrile and chloro-valeronitrile (C^5H^8ClN): the solution contains hydrochlorate of leucine (**Schwanert**).—5. *Sulphuric anhydride* is rapidly absorbed by leucine, forming a brown viscid liquid, which at 100° gives off carbonic and sulphurous anhydrides, and if then distilled with water, yields a fragrant liquid boiling at 97°, and forming crystalline compounds with the acid sulphites of the alkali-metals; probably, therefore, valeraldehyde (Schwanert).—6. Leucine heated for some time with a sufficient quantity of *nitric acid*, is completely resolved into gases, but so long as the decomposition is incomplete, the still remaining portion exhibits the characters of nitrate of leucine (Mulder).—7. When nitric oxide is passed into a solution of leucine in nitric acid, nitrogen is evolved, and leucic acid, $C^6H^{12}O^3$, is formed (Strecker, p. 575). The same acid is formed when chlorine is passed, not in excess, into a dilute solution of leucine in caustic soda (Gössmann). —8. Chlorine gas passed to saturation into a solution of leucine in carbonate of potassium, forms chloride of cyanogen, valerianic acid, and valeronitrile (Gössmann). —9. Leucine distilled with *peroxide of manganese* and dilute *sulphuric acid* yields valeronitrile and carbonic anhydride:

$$C^6NH^{13}O^2 + O^2 = C^5H^9N + CO^2 + 2H^2O.$$

When stronger sulphuric acid is used, valerianic acid passes over, and the residue contains ammonia. When leucine is distilled with *peroxide of lead* and water, only a trace of valeronitrile passes over, but a large quantity of butyral and then ammonia, which crystallise together in the form of butyral-ammonia.—10. By *permanganic acid* it is resolved into ammonia, oxalic acid, and valerianic acid (Neubauer, Ann. Ch Pharm. cvi. 59).—11. Leucine fused with *hydrate of potassium*, gives off ammonia and hydrogen and forms valerate of potassium (Liebig, Ann. Ch. Pharm. lvii. 127). 12. An aqueous solution of leucine emits a very offensive odour, and forms a peculiar acid, perhaps leucic acid (Cahours).—In a vacuum, the aqueous solution of leucine appears to remain undecomposed (Gössmann).—13. When a solution of 1 pt. of leucine in water is set aside for some weeks in contact with a quantity of moist *fibrin*, which in the dry state would weigh ½ pt., putrefaction takes place, the greater part of the leucine is decomposed, and ammonia is produced, together with such a quantity of valerianic acid as cannot be wholly produced from the fibrin. (Bopp.)

Combinations.—1. With acids. Leucine dissolves easily in acids, forming crystallisable salts. The *hydrochlorate*, $C^6H^{13}NO^2.HCl$, forms crystals very soluble in water. The *nitrate*, $C^6H^{13}NO^2.HNO^3$, called also *nitroleucic acid*, forms colourless needles. *Nitrate of leucine and barium* contains 41·01 per cent. baryta (Mulder). *Nitrate of leucine and calcium* forms mammellated groups containing water of crystallisation. *Nitrate of leucine and magnesium* forms small granular crystals. Leucine also forms a crystalline salt with *nitrate of silver*. These salts have probably the formula $C^6H^{13}NO^2.MNO^3$.

2. With bases. Leucine dissolves readily in caustic *alkalis*, but without neutralising them. The aqueous solution of leucine does not precipitate the solution of any metallic salt excepting basic acetate of lead.

Cupric salts.—Recently precipitated cupric oxide dissolves readily in aqueous leucine, forming a bluish liquid, which, on cooling, deposits crystalline grains or laminæ having the colour of ammoniacal sulphate of copper, and containing $Cu^2O.2C^6H^{13}NO^2$ or $C^{12}H^{24}C\overset{''}{cu}N^2O^4.H^2O$. (Gössmann.)

Lead-salts.—On cautiously adding ammonia to a boiling aqueous solution of leucine and neutral acetate of lead, nacreous scales are deposited containing $Pb^2O.2C^6H^{13}NO^2$ or $C^{12}H^{24}Ppb''N^2O^4.H^2O$ (Strecker, Ann. Ch. Pharm. lxxii. 89). Gössmann obtained a salt of the same composition; but in one experiment, perhaps in consequence of a peculiar degree of concentration, he obtained laminated groups of crystals resembling lepidolite, and containing $9Pb^2O.2C^6H^{13}NO^2$.

Mercuric salt.—Recently precipitated mercuric oxide dissolves very readily, and in considerable quantity in aqueous leucine; and the solution, when evaporated, deposits, first crystalline granules and afterwards laminæ containing 47·3 per cent. mercuric oxide: therefore $Hg^2O.2C^6NH^{13}O^2$ or $C^{12}H^{24}Hhg''N^2O^4.H^2O$. (Gössmann.)

Aqueous leucine is not precipitated by mercuric nitrate or chloride; but on addition of potash or ammonia, a white bulky precipitate is formed, which dissolves in excess of potash: the precipitate gradually becomes gelatinous and decomposes during washing (Gössmann). According to R. Hoffmann, on the contrary (Ann. Ch. Pharm. lxxxvii. 123), pure leucine is precipitated by mercuric nitrate in white flakes, without red colouring of the supernatant liquid, the production of such a colour indicating the presence of tyrosine.

Aqueous leucine added to a solution of *mercurous nitrate* throws down an abundance of white flocks, the supernatant liquid acquiring a red colour. (Braconnot.)

Pseudoleucine. This name is applied by Hesse (J. pr. Chem. lxx. 34) to a sulphuretted compound nearly related to leucine, found by A. Müller among the products of the decomposition of yeast (p. 579). It contains 3 or 4 per cent. sulphur, and is perhaps $C^{36}H^{73}N^6O^{12}S$. It is more soluble in alcohol than leucine, and when purified as completely as possible, forms a white spongy mass composed of shining laminæ. When cautiously heated, it sublimes almost without decomposition. It melts at 210°, and when distilled in an atmosphere of carbonic anhydride, yields, together with more volatile compounds containing nitrogen and sulphur, a woolly mass of acicular crystals resembling phlorizin, having the composition $C^6H^{11}NO$, and dissolving in dilute soda-ley with evolution of ammonia; this substance is designated by Hesse, leuconitrile. The other products of the dry distillation of pseudoleucine are sulphydric acid, hydrocyanic acid, a brownish, tarry, fetid substance, and several volatile bases, including ammonia, methylamine, dimethylamine, tritylamine, and a considerable quantity of amylamine.

LEUCITE. A silicate of aluminium and potassium, $(K\overset{'''}{Al})Si^2O^6$, occurring in monometric crystals, the usual form being the ikosi-tetrahedron or trapezohedron, hence called leucitohedron (*fig.* 180, ii. 125). Cleavage cubic, very imperfect; surface of crystals even, but seldom shining. The mineral often occurs disseminated in grains, rarely in granular masses. Hardness = 5·5 to 6. Specific gravity = 2·483 to 2·49. Lustre vitreous. Colour ash-grey or smoke-grey, white. Streak uncoloured. Translucent to opaque. Fracture conchoïdal. Brittle. Infusible before the blowpipe, except with borax or carbonate of calcium, with which it melts with difficulty to a clear globule. Gives a fine blue with cobalt-solution.

Analyses.—*a.* From Albano near Rome (Klaproth, *Beitr.* ii. 39).—*b.* From Pompeii (Klaproth, *ibid.*).—*c.* From Somma (Awdejew, Pogg. Ann. lv. 107).—*d.* From Vesuvius, eruption of 1811 (Rammelsberg, *ibid.* xcviii. 143).—*e.* From Vesuvius, eruption of 1845 (Rammelsberg, *ibid.*).—*f.* From Rieden on Lake Laach (Bischof, *Chem. Geologie*, ii. 2288):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Silica	54	54·5	56·05	56·25	57·34	56·22
Alumina	23	23·5	23·03	23·26	22·85	23·07
Potash	22	19·5	20·40	20·04	12·45	13·26
Soda	. .	. .	1·02	0·43	6·04	6·40
Lime	. .	. .	. .	0·32	0·20	0·23
Ferric oxide	. .	. .	. .	. .	0·14	0·48
Loss by ignition	. .	. .	. .	. .	0·59	
	99	97·5	100·50	100·30	100·11	99·66

The formula $(K\overset{'''}{Al}{}^2)Si^2O^6$ or $K^2O.Al^4O^3.4SiO^2$ requires 55·58 silica, 23·16 alumina, and 21·26 potash. The potash is sometimes replaced to a considerable extent by soda, as in *e.* and *f.* Abich found in a specimen from Vesuvius a still greater amount of soda.

Leucite occurs in volcanic formations, both ancient and modern; it is abundant in trachyte between Lake Laach and Andernach on the Rhine; the finest and largest crystals are, however, obtained from Vesuvius. Near Rome, at Borghetta on the north, and Albano and Frascate to the south, some of the older lavas appear to be almost entirely composed of it. This leucitic lava is used to form millstones, and millstones made of it have been discovered in the excavations at Pompeii.

Leucite occurs altered to felspar, nephelin, and kaolin. Leucite altered to glassy felspar has been observed on Somma by Scacchi. (Dana, ii. 231; Rammelsberg, *Mineralchemie*, p. 645.)

LEUCOCYCLITE. Syn. with APOPHYLLITE.

LEUCOHARMINE. Syn. with HARMINE.

LEUCOLINE. An organic base obtained from coal-tar, isomeric with chinoline, C^9H^7N. The two bases having this composition, the one obtained by the dry distillation of quinine and cinchonine, the other among those of the distillation of coal, were formerly thought to be identical, and the name chinoline was applied to both. Subsequent researches, however, having pointed out important differences between the two, especially in their behaviour with iodide of amyl, the base obtained from cinchonine is now distinguished as chinoline, and the coal-tar base (originally called *leucol* by Runge, who discovered it) as leucoline (see i. 869).

Each of these bases has a series of homologues corresponding with it, and differing in a similar manner from their isomers in the other series. The following names have been proposed by Greville Williams (Chem. Soc. J. xvi. 377) to distinguish the isomeric bases of the two series:

Coal series.		*Cinchonine series.*
Leucoline	C^9H^7N	Chinoline
Iridoline	$C^{10}H^9N$	Lepidine
Cryptidine	$C^{11}H^{11}N$	Dispoline

The higher homologues of chinoline, as far as $C^{16}H^{21}N$, have also been obtained; the corresponding bases in the leucoline series are at present unknown. (Proc. Roy. Soc. xiii. 312.)

LEUCOLITE. Syn. with Pycnite.

LEUCONE. $Si^4H^4O^5$.—A white substance obtained by the decomposition of silicone, $Si^4H^4O^3$, under the influence of light and water (Wöhler, Ann. Ch. Pharm. cxxvii. 268). See Silicium.

LEUCONIC ACID. *Oxycroconic acid*, $C^5H^8O^9$. (Will, Ann. Ch. Pharm. cxviii. 117; Lerch, *ibid.* cxxiv. 20.)—An acid produced from croconic acid (ii. 110) by oxidation and assumption of water:

$$C^5H^2O^5 + O + 3H^2O = C^5H^8O^9.$$

When a solution of croconate of potassium is treated with chlorine or nitric acid, it is decolorised and converted into leuconate of potassium, in the latter case with evolution of nitric oxide.

The acid [? prepared by decomposing the barium-salt with sulphuric acid] forms a colourless syrup, which when heated above 100° turns yellow, and is converted into croconic acid. It is tribasic, and forms white or pale yellow salts, which are unstable, being easily converted into croconates, especially in presence of alkalis. (Lerch.)

The *barium-salt*, $C^5H^5Ba^3O^9$, is obtained as a flocculent, yellowish-white precipitate by adding baryta-water to the solution of the potassium-salt, prepared as above, till it becomes alkaline. (Will.)

The *lead-salt*, $C^5H^5Pb^3O^9$, and the *silver-salt*, $C^5H^5Ag^3O^9$, are light-yellow precipitates.

Potassium-salt. When a solution of croconate of potassium decolorised as above with chlorine or nitric acid, is neutralised with caustic potash or carbonate of potassium, the liquid, just at the point of saturation, exhibits a transient play of colours, from colourless to purple-red, bluish-red and yellowish; and if the solution is concentrated, an abundant yellowish-white precipitate is formed at the same time, which redissolves in a large quantity of water. This precipitate was found by analysis to have the composition $C^5H^7KO^9$, but the lead-salt obtained from it by precipitation with acetate of lead exhibited the normal composition $C^5H^5Pb^3O^9$, whence it is probable that the sparingly soluble potassium-salt with 1 at. metal really consisted of the tripotassic salt mixed with free leuconic acid (Will). According to Lerch, the solution of the normal potassium-salt is decomposed by neutralisation with potash, yielding a small quantity of a black salt, probably dihydrocarboxylate of potassium (p. 190), together with oxalate and a colourless crystallised potassium-salt.

LEUCONITRILE. A product of the decomposition of pseudoleucine (p. 583).

LEUCOPHANE. A silicate of glucinum and calcium, occurring in syenite, together with albite, elæolite and yttrotantalite, on a small rocky islet near the mouth of the Langesundfiord in Norway, where it was found by Esmark. It is trimetric, with imperfect cleavage in three directions inclined to one another at angles of 53½° and 36½°, but usually occurs massive and columnar. Hardness = 3·5 to 4. Specific gravity = 2·974. It is more or less translucent, with pale dirty green or light wine-yellow colour, and yields a white powder, strongly phosphorescent when heated or struck. It likewise becomes electric when heated. It is optically biaxial. Before the blowpipe it melts to a clear bead with a tinge of violet, becoming turbid by flaming. Dissolves easily in borax to an amethyst-coloured glass; in phosphorus-salt it leaves a skeleton of silica; and with a small quantity of carbonate of sodium, it melts to a turbid bead, which, with a larger quantity of carbonate of sodium, sinks into the charcoal. With fused phosphorus-salt in an open tube, it gives the reaction of fluorine. According to an analysis by Rammelsberg (*Mineralchemie*, p. 764), it contains:

SiO^2	F	G^2O	Al^4O^3	Ca^2O	Mg^2O	Na^2O	K^2O	
47·03	6·57	10·70	1·03	23·37	0·17	11·26	0·30	= 100·43

with traces of ferric and manganous oxides, a composition which may be represented by the formula, $4NaF.3(2Ca^2O.2G^2O.3.SiO^2)$.

Melinophane, from the zircon-syenite of Norway, is nearly related in composition to leucophane.

LEUCOPHYLL. A colourless substance isomeric with chlorophyll, supposed by Sacc (Jahresber. 1859, p. 561) to be contained in those parts of plants which are capable of turning green, and to undergo this change under the influence of oxygen rendered active by the agency of light. The existence of such a substance is rendered probable, according to Sacc, by the fact that the plasma of those vegetable cells which quickly turn green on exposure to light, contains a substance which instantly assumes a bright verdigris-green colour when brought in contact with strong sulphuric acid, and that the same reaction is exhibited by the ready-formed light green granules of chlorophyll itself, whereas the plasma of cells which do not turn green in light, does not exhibit it.

LEUCOPYRITE. Native proto-arsenide of iron, $FeAs$ or $FfeAs^2$, also called *arsenosiderite* (see p. 368).

LEUCORCEÏN. An ammoniacal solution of orceïn slightly acidulated with hydrochloric acid, is completely decolorised by immersing a piece of zinc in it. If ammonia be then added, a white precipitate called leucorceïn is formed, which on exposure to the air becomes violet, and finally purple. (See ORCEIN.)

LEUCOTURIC ACID. Laurent's *Oximide.* (Schlieper, Ann. Ch. Pharm. lvi. i.)—Formed when an aqueous solution of alloxanic acid (i. 138) is rapidly boiled down to a syrup: cold water is then added, which leaves the leucoturic acid undissolved. It is a white crystalline powder, insoluble in cold water, slowly but rather abundantly soluble in boiling water, whence it crystallises on cooling. It is readily soluble in aqueous alkalis, hence it is precipitated by mineral acids, and by the aid of heat decomposes alkaline carbonates. The potash-solution is decomposed by keeping or by gentle heat, ammonia being evolved, and oxalic acid formed abundantly. The ammonia-solution yields on evaporation crystals of the ammonium-salt, whose solution precipitates nitrate of silver. Leucoturic acid is not decomposed by boiling with strong nitric acid. It appears to be monobasic. Schlieper found it to contain 31·15 per cent. carbon, 2·80 hydrogen, and 24·51 nitrogen, whence he deduced the formula $C^6H^3N^2O^6$, requiring 31·30 carbon, 2·61 hydrogen, 24·35 nitrogen, and 41·74 oxygen. Gerhardt pointed out the improbability of this formula, as it contains an uneven number of atoms of hydrogen and nitrogen. Baeyer suggests the formula $C^6H^4N^4O^5$, which requires 33·98 per cent. carbon, 1·89 hydrogen, 26·41 nitrogen, and 37·72 oxygen. F. T. C.

LEVOLUSAN or **LÆVULOSAN.** A product of the decomposition of cane-sugar by heat, having a lævo-rotatory power of 15° for the transition-tint (ii. 864).

LEVIGATION. The mechanical process of grinding the parts of bodies to a fine paste, by rubbing them between the flat face of a stone called the muller, and a table or slab called the stone. Some liquid is always added in this process. The advantage of levigation with a stone and muller over that of triturating in a mortar is, that the materials can more easily be scraped together and subjected to the action of the muller, than in the other case to that of the pestle; and, from the flatness of the two surfaces, they cannot elude the pressure. U.

A figure and description of a mill for levigating litharge are given under LEAD (p. 514).

LEVYNE. A hydrated silicate of calcium and aluminium, occurring in rhombohedral crystals truncated by the basal face oR, which greatly predominates, and always in twins compounded parallel to oR. Angle R : R = 106° 4′; oR : R = 136° 1′; ratio of principal to secondary axes = 0·8358 : 1. The crystals are often striated and often in druses. Hardness = 4 to 4·5. Specific gravity = 2·09 to 2·16. Lustre vitreous. Colourless, white, reddish or yellowish. Transparent to translucent. Before the blowpipe it melts to an opaque blebby glass. When pulverised it dissolves in acids without gelatinising.

Analyses. *a. b.* from Faroë, by Berzelius; *c.* from Skye, by Connel; *d.* from Ireland, by Damour (*Rammelsberg's Mineralchemie*, p. 802):

	SiO^2	Al^4O^3	Ca^2O	Na^2O	K^2O	Mg^2O	H^2O		
a.	48·00	20·00	8·35	2·86	0·41	0·40	19·30	=	99·32
b.	47·50	21·40	7·90	4·80	. .	. .	18·19	=	99·79
c.	46·30	22·47	9·72	1·55	1·26	. .	19·51	=	100·81
d.	44·48	23·77	10·71	1·38	1·61	. .	17·41	=	99·36

Berzelius' analysis gave the formula of chabasite. Damour's, which contains less silica than the rest, leads to the formula:

$$Ca^2O.Al^4O^3.3SiO^2 + 4H^2O \text{ or } (Ca^2\overline{Al}^2H^4)Si^3O^{12}.2H^2O,$$

which is that of a hydrated orthosilicate.

Levyne is found in amygdaloïd at Glenarm; on Hatfield Moss, Renfrewshire; at Dalanyfren, Faroë; at Godhavn, Disco Island, Greenland; and at Skagastrand in Iceland.

LHERZOLITE. A variety of augite from Lake Lherz in the Pyrenees, where it occurs both crystallised and lamellar, and of a deep-green or olive-green colour.

LIATRIS. According to W. Procter, jun. (Am. J. Pharm. xxxi. 556), cumarin occurs in microscopic prisms on the dried leaves of *Liatris odoratissima*, a plant growing in the Southern States of North America.

LIBETHENITE. A native phosphate of copper, $4Cu^2O.P^2O^5$ + aq. or $Cu^3PO^4.CuHO$, found at Libethen in Hungary, and other localities. (See PHOSPHATES.)

LICHENIC ACID. See Fumaric acid (ii. 741).

LICHENIN. $C^6H^{10}O^5$. (Gm. xv. 119.)—A substance isomeric with starch, occurring in several species of moss and lichen, especially in the so-called Iceland moss (*Cetraria islandica*), which is really a lichen. According to Maschke (J. pr. Chem. lxi. 7), it is formed from starch by the action of the free acid in the plant. It is extracted from Iceland moss by macerating the chopped lichen for twenty-four hours with a large quantity of cold water containing a small quantity of carbonate of sodium, and continuing the treatment till the liquid no longer tastes bitter. It is then boiled with water, and the boiling decoction is strained through a linen cloth. The liquid on cooling coagulates to a kind of jelly, which dries up to a hard brittle mass (Berzelius). Payen removes the bitter matter by washing the lichen successively with ether, alcohol of specific gravity 0·83 and 0·90, cold water, very weak solution of carbonate of sodium, aqueous hydrochloric acid of the strength of 1 per cent., and pure water. Davidson (Ed. N. Phil. J. xxviii. 260) macerates 112 lbs. of Iceland moss for a fortnight with potash-ley prepared from 4 lbs. of pearlash, or for six days with milk of lime prepared from 6 lbs. of lime, then washes with dilute hydrochloric acid, and finally with water. Chloride of lime may also be used for the maceration. Knop and Schnedermann (Ann. Ch. Pharm. lv. 164) treat Iceland moss with a large quantity of hydrochloric acid, and precipitate the solution, after dilution and straining, with alcohol. The precipitated lichenin is then freed from water and rendered friable by repeated treatment with absolute alcohol, and freed from adhering hydrochloric acid by immersion in running water.

Lichenin in the dry state forms a hard brittle mass, tasteless, but having a faint odour resembling that of lichens. In cold water it swells up without dissolving, dissolves in boiling water, and is deposited in the form of a jelly; by prolonged boiling, however, it loses the property of gelatinising, and is converted into a gummy substance, probably dextrin. When the solution in boiling water is left to evaporate, the lichenin separates as a rough pellicle on the surface. Lichenin is insoluble in alcohol and ether.

Dilute acids dissolve lichenin and convert it into glucose. *Nitric acid* heated with it converts it into oxalic acid. Pure lichenin is merely coloured yellow by *iodine*; but a green or blue colour is often produced, from admixture of starch.

LICHENS. The following enumeration of the proximate constituents of lichens is given by Rochleder in *Gmelin's Handbuch*, viii. 94:

Bæomyces roseus, Pers. See analysis by Brandes. (Berl. Jahrb. xxv. 1, 38.)

Biatora lucida, Fr. Contains usnic acid. (Knop, Götting. gelehrte Anzeigen, 1843, 2 u. 3 Stück, 16; and Ann. Ch. Pharm. xlix. 103.)

Cetraria aculeata, Fr. Contains no cetrarin, but moss-starch (lichenin) and lichenic (fumaric) acid. (Weppen, Pharm. Centr. 1838, No. 12.)

Cetraria islandica, Ach. Contains: fumaric acid (Schödler, Ann. Ch. Pharm. xvii. 87) and cellular substance; starch not deposited in granules, but uniformly distributed among the cells (lichenin); cetraric acid, lichenstearic acid, tallochlore, fat, sugar, gum, yellow extractive matter, a brown substance formed from cetraric acid, and a body not exactly determined (Knop and Schnedermann, lv. 144). This lichen always contains alumina (Knop, J. pr. Chem. xxxviii. 347). It contains a large quantity of a carbohydrate (lichenin) convertible into sugar. (C. Schmidt, Ann. Ch. Pharm. li. 29).

Cladonia digitata, Hoffm.
Cladonia macilenta, Hoffm. } contain starch. (Knop, *loc. cit.*)
Cladonia uncinata, Hoffm.

Cladonia pyxidata, Spr. Contains a large quantity of a carbohydrate convertible into sugar. (C. Schmidt, *loc. cit.*)

Cladonia rangiferina, Hoffm. (*Lichen rangiferina*, L.) Contains usnic acid (Rochleder and Heldt, Ann. Ch. Pharm. xlviii. 13), and a large quantity of carbohydrate convertible into sugar. (C. Schmidt, *loc. cit.*)

Evernia furfuracea, Mann. (*Parmelia*, Ach.) Contains usnic acid (Rochleder and Helot, *loc. cit.*). See an analysis of this lichen grown on a pine-tree, by John. (Chem. Schr. vi. 41.)

Evernia ochroleuca, Fr. (*Parmelia sarmentosa*, Ach.) Contains usnic acid. (Knop, *loc. cit.*)

Evernia prunastri, Ach. Contains usnic and evernic acids (Stenhouse, Phil. Mag. [3] xxxii. 300). Rochleder and Heldt found lecanoric, but not a trace of usnic acid.

Evernia vulpina. The experiments of Bebert (Ann. Ch. Pharm. ii. 342) on the so-called vulpulin, seem to show that this lichen contains chrysophanic acid. (Berzelius, Jahresber. xii. 256.)

Gyrophora pustulata, Ach. (*Umbelliaria*, Hoffm.) From Norway. Contains gyrophoric acid. (Stenhouse, Phil. Trans. 1849, p. 458.)

Isidium corallinum, Ach. Contains a large quantity of oxalate of calcium. (Braconnot, Ann. Ch. Phys. [2] xxviii. 319.)

Lecanora Parella, Ach. (*Parmelia*, Schaer.) Contains: three fats, tannin, parellic acid, lecanoric acid, chlorophyll, and gum, which gives a greenish-blue colour with iodine (Schunck, Ann. Ch. Pharm. liv. 257). The several species of *Lecanora* contain lecanoric acid. (Schunck, *ibid.* xli. 157.)

Lecidia candida, Ach. (*Psora*, Dec.) Contains a large quantity of oxalate of calcium. (Braconnot, *loc. cit.*)

Lecidia geographica, Schaer. From the Brocken. Contains usnic acid. (Knop, *loc. cit.*)

Parmelia ciliaris, Ach. (*Borrera ciliaris.*) See analysis by John. (Chem. Schr. vi. 39.)

Parmelia parietina, Ach. Contains chrysophanic acid, a yellow non-crystallisable colouring matter (Rochleder and Heldt, *loc. cit.*), and a carbohydrate convertible into sugar (C. Schmidt, *loc. cit.*) This lichen contains: a yellow and a red colouring matter, wax, crystalline stearin, chlorophyll, soft resin, gum, lichenin, vegetable mucilage, sugar, extractive matter, traces of volatile oil, and phosphate of calcium (Hesberger, Buchn. Repert. xlvii. 179); compare Sander (*Ueber die Wandflechte*, Sondershausen, 1815; and Kastn. Arch. viii. 431); Monnhardt (*Dissert. sist. Lobariæ parietinæ Analysin chem.* Kieloniæ, 1818); Schröder (Berl. Jahrb. 1819, p. 44); Markowitz (Scher. Ann. i. 438); Thomson (Ann. Ch. Pharm. liii. 252 and 260).

Parmelia physodes, Ach. Contains crystallised physodin. (Gerding, *Arch Pharm.* lxxxvii. 1.)

Parmelia saxatilis, Ach. Contains a small quantity of carbohydrate convertible into sugar. (C. Schmidt, *loc. cit.*)

Patellaria hæmatoma, Hoffm. (*Parmelia*, Ach.—*Patellaria rubra*, Hoffm.—*Parmelia*, Ach.—*Patellaria ventosa*, Dec.—*Parmelia*, Ach.) Contain large quantities of oxalate of calcium (Braconnot, *loc. cit.*). *P. hæmatoma* and *P. ventosa* contain usnic acid. (Knop, *loc. cit.*)

Patellaria tartarea, Dec. (*Parmelia*, Ach.) Contains large quantities of oxalate of calcium (Braconnot, *loc. cit.*) In a specimen from Norway, Stenhouse (*loc. cit.*) found gyrophoric acid. See analysis by N. v. Eserbeck (Ber. Arch. xvi. 135).

Peltigera canina, Hoffm. Contains a carbohydrate convertible into sugar. (C. Schmidt, *loc. cit.*)

Pertusaria communis, Dec. Contains a large quantity of oxalate of calcium.

Placodium ochroleucum, Dec. (*Parmelia saxicola*, Ach.) and *Placodium radiosum*, Dec. (*Parmelia radiosa*, Ach.) Contain very large quantities of oxalate of calcium. (Braconnot, *loc. cit.*)

Ramalina calicaris, Fr. var. *fastigiata*. Contains large quantities of starch, colouring matter and bitter substance, and a small quantity of saccharic acid (Berzelius, Scher. Ann. iii. 97). Contains usnic acid. (Rochleder and Heldt, *loc. cit.*)

Ramalina calicaris, Fr. var. *fraxinea*. The ash contains a large quantity of ferric oxide, but scarcely a trace of potash (John, Chem. Schr. vi. 37); soluble and coagulable albumin (Berzelius, Scher. Ann. iii. 208); lichenin, and usnic acid (Rochleder and Helot, *loc. cit.*)

Roccella Montagnei, Belen. Contains erythric acid. (Stenhouse, *loc. cit.*)

Roccella tinctoria, Ach. This lichen (var. *fuciformis*, from Angola and Madagascar) contains erythric acid (Heeren's erythrin, Kane's erythrilin, ii. 502), a fatty substance, roccellic acid, a brown substance extractable by potash, chlorophyll, and ash-constituents (Schunck, Phil. Mag. J. [3] xxix. 194). *Roccella tinctoria* from South America was found by Stenhouse (Phil. Mag. [3] xxxii. 300) to contain α-orsellic acid; the same lichen from the Cape of Good Hope contained β-orsellic acid and roccellinin. Stenhouse and Scouler are of opinion that the *Roccella tinctoria*, var. *fuciformis* analysed by Schunck, was really *R. Montagnei.*

Squamaria elegans, Fée. Contains chrysophanic acid. (Thomson, Ann. Ch. Pharm. liii. 266.)

Squamaria lentigera, Dec. (*Parmelia*, Ach.) Contains a very large quantity of oxalate of calcium. (Braconnot, *loc. cit.*)

Sticta pulmonacea, Ach. Contains lichenin and a bitter principle (Weppen, Pharm. Centr. 1838, No. 12) very near cetraric acid in composition, and named stictic acid by Knop and Schnedermann (J. pr. Chem. xxxix. 303); compare John (Chem. Schr. vi. 39).

Ulceolaria esculenta, Ach. Contains a large quantity (13 per cent.) of gum. (Kirchhoff, Scher. Ann. iii. 213.)

Ulceolaria scruposa contains a large quantity of oxalate of calcium (Braconnot, *loc. cit.*)

Usnea barbata, Fr. Contains usnic acid (Rochleder and Heldt, *loc. cit.*), and lichenin. (Berzelius, Scher. Ann. iii. 205.)

Usnea barbata, Fr. var. *florida*. (*Usnea florida*, Hoffm.) Contains usnic acid (Knop, *loc. cit.*), and a small quantity of carbohydrate convertible into sugar. (C. Schmidt, *loc. cit.*)

Usnea hirta, Hoffm. (*U. barbata* var. *plicata*, Fr.) Contains usnic acid (Knop, *loc. cit.*), bitter principle, gum-sugar, lichenin and a soft skeleton (Berzelius, Scher. Ann. iii. 203). Contains a large quantity of carbohydrate convertible into sugar. (C. Schmidt, *loc. cit.*)

Variolaria amara, Ach. Contains picrolichenin (Alms, Pharm. Zeit. 1832, No. 2, 17; Ann. Ch. Pharm. l. 61.) Contains chlorophyll, and a colourless, crystallisable, bitter substance, forming with ammonia a red non-bitter resin (Gregory, J. Pharm. Juin 1835, p. 314; Pharm. Centr. 1835, No. 39). Contains picrolichenin, two resins, chlorophyll, gum-sugar, bitter extractive matter, oxalate of calcium, silicic acid, iron and cellulose (A. Müller, Pharm. Centr. 1844, No 47); compare Filhol and Bouchardt. (J. de Méd. de Toulouse, vii. 201, and Pharm Centr. 1844, No. 39.)

Variolaria communis, Ach. (grown on a lime-tree). Contains waxy matter, green colouring matter, a bitter and acrid principle, uncrystallisable sugar, oxalate of calcium (4·7 per cent.), a substance resembling animal gelatin, &c. (Braconnot, Ann. Chim. Phys. [2] vi. 132.)

Variolaria dealbata, Dec. (*Lichen dealbatus*, Ach.) See analysis by Robiquet (Ann. Ch. Phys. [2] lxii. 236), who found variolaria in this lichen, and prepared orcin from it.

On the colouring matters of lichens, see Archil, Erythric acid, Evernic acid, Gyrophoric acid, Lecanoric acid, Litmus, Orsellic acid, Orcin, Usnic acid, Variolarin.

LICHENSTEARIC ACID. $C^{14}H^{24}O^3$. (Schnedermann, and Knop, Ann. Ch. Pharm. lv. 149.)—An acid existing in Iceland moss (*Cetraria islandica*), and probably also in the fly-agaric or toadstool (*Agarious muscarius*) (Bolley, Ann. Ch. Pharm. lxxxvi. 50). To prepare it, Iceland moss is boiled for a quarter of an hour in alcohol containing carbonate of potassium; the strained decoction is mixed with excess of hydrochloric acid; and the whole is diluted with 4 or 5 volumes of water. The precipitate thereby formed is washed with water, and afterwards boiled three or four times with alcohol of 42 to 45 per cent. On cooling the alcoholic solution, a mixture of lichenstearic and cetraric acids with a third substance, is separated, from which the lichenstearic acid is taken up by boiling rock-oil, and again deposited on cooling, or more completely on partial distillation. Purification is effected by recrystallising from alcohol, with the help of animal charcoal.

Properties.—The acid forms a loose, white mass, consisting of delicate crystalline laminæ having a pearly lustre. From a solution in very dilute alcohol it is obtained in small rhombic tables; on concentrating the solution, partly in oily drops. It is inodorous, has a rancid, harsh, not bitter taste, melts at about 120° without loss of weight, and solidifies to a crystalline mass; is not volatile.

It is perfectly insoluble in *water*, but dissolves readily in *alcohol*, *ether*, and *oils*, both fixed and volatile.

The *salts* of lichenstearic acid are permanent in the air, and are decomposed by acids, with separation of lichenstearic acid. Their solutions froth up on boiling.

Ammonium-salt.—The easily prepared solution of the acid in warm aqueous ammonia forms, on cooling, a white, elastic jelly, appearing under the microscope to contain a quantity of long, extremely delicate crystals. The salt, when dry, is white and silky, and only partially soluble in warm water, with loss of ammonia.

The *barium-salt*, $C^{14}H^{23}BaO^3$, is obtained, on precipitating aqueous lichenstearate of sodium with a soluble barium-salt, as a greyish-white precipitate, which cakes together in boiling water.

The *lead-salt*, $C^{14}H^{23}PbO^3$, is obtained, by precipitating the aqueous sodium-salt with neutral acetate of lead, in white flakes, which, on boiling the liquid, melt to a yellow, semi-fluid mass. It is brittle, softens between the fingers, and becomes semi-fluid at 100°, at which temperature also it appears to decompose.

Potassium-salt.—A solution of the acid in aqueous carbonate of potassium throws down, when concentrated by evaporation, yellowish flakes, which are soluble in water, but insoluble in alkaline liquids. If the solution be evaporated to dryness, and the residue extracted with boiling absolute alcohol, a part of the salt is obtained, on cooling, as an indistinctly crystalline powder; and the remainder, on concentrating the solution, in the form of a syrup. It dissolves easily in water, forming an alkaline liquid, which tastes like soap, and froths up on boiling.

The *silver-salt* is thrown down from a solution of the sodium-salt, by nitrate of silver, as a greyish-white precipitate, turning violet on exposure to light, and caking together in boiling water. It decomposes below 100°.

The *sodium-salt* is obtained in the same manner as the potassium-salt. A concentrated aqueous solution throws down white granules on standing.

LIEBENERITE. A silicate found in a red felspar porphyry on Mount Viesena, Fleimser valley, Tyrol, crystallised in six-sided prisms, without distinct cleavage. Hardness = 3·5. Specific gravity = 2·18. Colour greenish-grey. Fracture splintery. Before the blowpipe it whitens and intumesces, but does not fuse. Contains, according to Marignac (Bibl. univ. iv. 157), 44·66 per cent. silica, 36·51 alumina, 1·94 ferric oxide, 1·40 magnesia, 9·90 potash, 0·92 soda, and 5·05 water (= 100·38). Marignac regards it as pinite (*q.v.*); according to Blum, Breithaupt, and Haidinger, it is a pseudomorph of nephelin. It has also been regarded as an altered dichroïte. (Dana, ii. 226; Rammelsberg's *Mineralchemie*, p. 837.)

LIEBIGITE. Calcio-uranic carbonate. See CARBONATES (i. 798).

LIENIN. A substance containing 53·71 per cent. carbon, 8·95 hydrogen, 4·82 nitrogen, and 32·52 oxygen, found by Scherer (Jahresber. 1851, p. 597) in the fluid of the spleen.

LIEVRITE. *Ilvaite. Yenite.*—A silicate of iron and calcium, occurring in trimetric crystals in which $\infty P : \infty P = 110^\circ\ 12'$; $oP : \bar{P}\infty = 146^\circ\ 20'$; ratio of principal axis, brachydiagonal and macrodiagonal = 0·66 : 1 : 1·46. Observed combination, $\infty P . P . \infty\bar{P}2 . \infty\breve{P}2 . \infty\breve{P}3 . \infty\breve{P}4 . \infty\bar{P}\infty . \infty\bar{P}\infty . P . 3\breve{P}\infty . 2\breve{P}\infty . \frac{1}{3}\bar{P}\infty . 2\breve{P}2$. Lateral faces usually striated longitudinally. Cleavage parallel to the longer diagonal, indistinct. Also columnar or compact massive. Hardness = 5·5 to 6. Specific gravity = 3 8 to 4·2. Lustre submetallic. Colour black, of various shades. Streak black, inclining to grey or brown. Fracture uneven. Brittle. Before the blowpipe it melts easily to a magnetic globule. It is easily and completely decomposed by hot hydrochloric acid.

Analyses: 1. Stromeyer (*Rammelsberg's Mineralchemie*, p. 740).—2. Rammelsberg (*ibid.*).—3. Wackernagel (*ibid.*):

	SiO^2	Fe^4O^3	Fe^2O	Mn^2O	Ca^2O	Al^4O^3	H^2O		
1. Elba.	29·28	23·00	31·90	2·43	13·78	0·61	1·27	=	101·27
2. „	29·83	22·55	32·40	1·50	12·44	. .	1·60	=	100·32
3. „	29·45	25·79	28·60	0·94	15·49	. .	. .	=	100·27

These results do not agree very closely with any simple formula, but they may be approximately represented by $9M^2O.2Fe^4O^3.6SiO^2$.

Lievrite occurs in the Island of Elba, in large solitary crystals and aggregated crystallisations in compact augite. It is also found at Fossum and Skeen in Norway; in Siberia; near Andreasberg in the Hartz; near Predazzo, in the Tyrol, in granite; at Schneeberg, in Saxony; and near Bytown, Canada.

Kobell's *Wehrlite*, a massive granular mineral from Szurraskö in Hungary, containing 34·60 per cent. silica, 0·12 alumina, 42·38 ferric oxide, 15·78 ferrous oxide, 0·28 manganous oxide, 5·84 lime, and 1·00 water, is sometimes regarded as lievrite. It is, however, harder (hardness = 6 to 6·5), fuses with difficulty and only on the edges, and is but imperfectly soluble in acids. (Dana, ii. 263.)

LIGHT. Light is the agent which makes us acquainted with the existence of bodies through the organ of sight. It is likewise one of the most important agents of chemical change. Plants, with few exceptions, are absolutely dependent upon it for their existence and development; the greater number of animals are incapable of living in health and vigour unless subjected to its influence; and a variety of chemical processes both natural and artificial depend in great measure upon its agency.

The several views which have been entertained respecting the nature of light may be ranged under two heads, the system of emission, and the system of undulations. The former, suggested in ancient times by Empedocles and Democritus, afterwards adopted by Gassendi, and brought to the utmost degree of completeness of which it is susceptible by Newton, supposes light to consist of minute particles emitted from luminous bodies, and travelling through space with immense rapidity till they reach the eye. The latter theory, the germ of which may be found in the writings of Aristotle, supposes that objects are rendered visible by vibrations excited by luminous bodies in an elastic medium, called the ETHER, pervading all space, and filling up the intervals between the molecules of ponderable bodies. Ideas similar to this were advocated by Descartes, Mallebranche, and Grimaldi; but it was in the hands of Huyghens that the theory first assumed a definite shape, and was rendered capable of affording an exact explanation of known facts; and by the subsequent labours of Young, Fresnel, Cauchy, and others, it has been brought to such a state of perfection that it is capable of accounting for most of the phenomena of light in their minutest details, and has even anticipated many important results, subsequently confirmed by observation; whereas the theory of emission, though it gave a satisfactory account of most of the phenomena known in Newton's time, is altogether unable to account for a vast number of facts which have since been discovered. The wave-theory is therefore now universally accepted as the true representative of the phenomena.

The existence of a fluid or medium, such as the theory supposes to exist in the celestial spaces, may be regarded almost as a matter of certainty: for the motions of comets are found to be retarded in a manner which cannot be accounted for on any other hypothesis. This phenomenon has been particularly studied in the case of Encke's comet, which revolves about the sun in a period of three years. Now this period is found to be continually diminishing, showing that the comet is gradually approaching the sun, an effect which can only be accounted for by supposing its motion to be retarded by the action of a resisting medium. Moreover, as the light-waves are transmitted freely, not only through the celestial spaces, but also through air, water, glass, and other transparent media, we must likewise suppose that the spaces between the molecules of these bodies are filled up by the ether. It will hereafter be shown that the elasticity of the ether is different in different media.

In the present article, after speaking of the sources of light, we shall endeavour to show how the wave-theory is applied to explain the several phenomena of Radiation, Interference, Reflection, Refraction, Absorption, and Polarisation.

The chemical action of light will be treated in a separate article.

Sources of Light.

The sun, the fixed stars, certain meteors, and terrestrial bodies in the states of incandescence and phosphorescence, shine by their own light; all other bodies, terrestrial or celestial, are visible only when the light of a self-luminous body falls upon them. Our knowledge of the peculiar conditions which render bodies self-luminous is not very exact; but assuming that vision is produced by undulations in an all-pervading elastic medium, we must suppose that these undulations are excited by vibratory movements in the particles of luminous bodies. This supposition is moreover in accordance with the conclusions deduced from the phenomena of heat (p. 131). The particles of all bodies are supposed to be in a state of constant motion, and it depends upon the intensity and rapidity of this motion whether the effect produced on our senses by the undulations thereby excited in the surrounding ethereal medium, is that of heat alone, or of heat accompanied by light. We shall see hereafter that the non-luminous heat-waves are of less rapid vibration than those which likewise produce light. Accordingly when the temperature of a body is gradually raised, it first gives out heat unaccompanied by light; but at a certain temperature, the vibrations become rapid enough to excite in the ethereal medium, waves which produce in our organs the sensation of red light, and at still higher temperatures vibrations are produced of a rapidity corresponding to those which excite the sensation of yellow and of blue light, which, together with the red, produce the combined sensation of white light. (See RADIATION OF HEAT.)

A body may be raised to the temperature necessary to render it luminous, either by chemical action (combustion) going on within its own mass (*e. g.* the burning of metals, wood, hydrocarbons, &c.), or by heat imparted to it from without, as by the combustion of a neighbouring body, by the electric current, by mechanical agency such as friction or percussion, or by the sun's rays concentrated upon it by a lens or mirror. Matter in either of the three states of solid, liquid, and gas, may be brought to the incandescent or self-luminous state; flame, indeed, is merely incandescent gas; but, as explained in the article COMBUSTION (i. 1094), solids become luminous at a much lower temperature than gases, and give out much more light at any given temperature: hence the brightest flames are those which contain suspended particles of solid matter raised to a very high temperature by the heat of the combustion.

The light of the sun and of the fixed stars is in all probability due to incandescence; indeed recent observations have shown that the luminous atmosphere of the sun contains many of the metals which exist in our own globe, and similar observations have been made on several fixed stars.

Phosphorescence.—Many bodies, under peculiar circumstances, are thrown into such a state of vibration that they emit light without perceptible evolution of heat. Phosphorus, in the state of slow combustion which takes place on exposing it to the air at ordinary temperatures, gives off acid vapours, which shine in the dark with a faint bluish light: hence the term *phosphorescent* has been extended to all bodies which exhibit a similar luminosity, from whatever cause it may arise. The phosphorescence of decayed bodies of plants and animals, as of dead wood and putrid sea-fish, is familiar to every one. The flowers of certain living plants, especially those of a bright yellow or red colour, as *Calendula officinalis*, *Tropæolum majus*, *Helianthus annuus*, and

Papaver orientale, have been observed to emit a sudden flashing light on fine summer evenings, a little after sunset. Some plants also emit in the dark a faint continuous light, probably arising from the combustion of some substance, such as a hydrocarbon, emitted from them; this phenomenon has been observed in the leaves of *Phytolacca decandra*, which shine at night, sometimes with bluish-green, sometimes with yellowish-green light. The acrid milky juice of *Cipo de Cananum* (a Brazilian plant, probably of the euphorbiaceous order) emits light for several hours, after flowing from a wound in the plant. *Rhizomorpha subterranea*, a plant which grows in mines, emits light from its whole surface, but especially from the whitish growing points, and a similar phenomenon has been observed in other subterranean plants.

A more familiar kind of phosphorescence is that exhibited by many living animals, as by the glow-worm and fire-fly, and the numberless small marine animals, such as crustacea, medusæ, polypora, and infusoria, which give rise to the phosphorescence of the sea at night. In many animals the phosphorescence is an act of the will; in others it takes place at a particular period of life.

In nearly all phosphorescent plants and animals, the phosphorescence appears to be due to chemical action, in fact to a slow combustion: for it increases in brightness in pure oxygen gas, and ceases altogether in a vacuum or in nitrogen or carbonic acid gas; the phosphorescence of decaying fish, however, takes place in nitrogen as well as in air or oxygen.

Phosphorescence may be excited artificially in a large number of bodies by any cause which sets their particles in rapid vibration; viz., by *heat*, by the *electric discharge*, by *mechanical action*, and by *insolation*.

1. Many solid bodies become phosphorescent when thrown upon a heated surface; such is the case with diamond, chalk, certain varieties of fluor-spar, oyster-shells, paper, flour, especially that of maize, and indeed with most well-dried organic substances. This effect is not to be confounded with incandescence, for it takes place at temperatures much below an ordinary red heat; and the light emitted is generally of a blue or violet tint, instead of the dull red of incipient incandescence.

2. A lump of sugar through which a powerful electric discharge is passed, shines for several seconds afterwards with a beautiful violet light; and a similar effect is produced on many non-conducting minerals, but not on metals or other substances of good conducting power. Substances which have lost the faculty of becoming phosphorescent by heat or by insolation, recover it after they have been subjected to repeated electric discharges. There can be but little doubt that the immediate effect of the discharge is to throw the particles of the body into a state of rapid vibration, which is then communicated to the surrounding ethereal medium.

3. The phosphorescence produced by friction, percussion, and other mechanical actions, generally lasts only as long as the disturbing cause continues to act. In many cases a development of electricity takes place at the same time, and to this the light may be partly or in some cases wholly due; sometimes, however, the light emitted appears to be a direct consequence of the vibratory motion communicated to the particles by the mechanical disturbance. Adularia struck with a hammer so as to split it, emits at each crack a light which may last for several minutes; and when ground in a mortar, it appears all on fire. Quartz, fluor-spar, rock-salt, and sugar likewise exhibit light when broken or pounded.

Light is often emitted during the change of state of bodies, especially in the passage from the amorphous to the crystalline state, and the separation of crystals from a solution (i. 200).

4. *Insolation*, or exposure to the sun's rays, develops phosphorescence most easily in substances which are bad conductors of heat. Most calcareous substances are capable of becoming phosphorescent by insolation: *e.g.* carbonate and sulphate of calcium, fluor-spar, petrifactions, shells, and pearls.

Canton's phosphorus, prepared by heating calcined oyster-shells with sulphur, emits after insolation a yellow light bright enough to show the time by a watch. The phosphorescence may even be excited by exposure to the light of a candle. The *Bolognian phosphorus*, prepared by strongly igniting heavy spar with gum-tragacanth, emits, after insolation, a bright light which lasts for more than a day. *Baudoin's phosphorus* (fused nitrate of calcium) emits a white light. Diamonds sometimes remain phosphorescent for an hour, after exposure to the sun for a few seconds only. Certain organic substances, *e.g.* flour, sugar, gum, white wax, and resin, also shine after insolation.

From recent researches by E. Becquerel, it appears that the number of bodies rendered phosphorescent by insolation, is much larger than has hitherto been supposed, phosphorescence, lasting for a few seconds, or rarely for a few minutes, being exhibited by numerous minerals and salts, chiefly with alkaline or earthy bases. (See *Daguin's Traité de Physique*, iv. 250.)

For numerous details relating to phosphorescence, see *Gmelin's Handbook* (i. 181—209).

The Electric Light.—The passage of electricity, when it meets with a certain resistance, is accompanied by light, more or less bright in proportion to the strength of the charge and the degree of resistance. As the discharge in all cases, even in the most highly rarefied atmospheres, such as Gassiot's tubes (ii. 391), takes place through the medium of material particles, we may suppose in this case also that the light owes its origin to vibrations excited in these particles by the electric action.

Radiation.

To understand the manner in which the vibrations of luminous bodies are transmitted in waves or undulations through the surrounding ether, it will be necessary to consider shortly the nature of undulations in general. A *wave* or *undulation* is a disturbance excited in one part of a body, and communicated to the other parts in regular succession. For example, a stone thrown into water depresses the water at the part where it is thrown in; the portion so depressed exerts a lateral pressure on those immediately surrounding it; and these again exert an upward pressure on the particles external to them, and form a raised circle; afterwards these portions fall, and in falling, push up other particles, situated external to them, and thus the undulation continually spreads outwards in concentric circles till it extends to the whole surface of the liquid. Now it is important to notice that these particles have no progressive motion; they merely move up and down, as may be seen by observing the motion of a light body floating on them: there is an appearance of progressive motion, but it is only an appearance, arising from the same form or state of motion being successively communicated to the different parts of the liquid. The wave travels onwards, perhaps for miles, or, as in the case of the ocean tide-wave, all round the globe; but the individual particles of water merely move in vertical lines through spaces not exceeding a few feet. Again, in the case of the waves in air which produce sound, the individual particles of air merely move backwards and forwards through small intervals, the motion being first excited in the particles immediately in contact with the sounding body, afterwards communicated by these to the next, and so on, and this communication of the vibratory motion from particle to particle constitutes a wave of sound. Here again the progress of the wave must be carefully distinguished from the motion of the individual particles. Sound travels through the air at the rate of about 1100 feet in a second; now if the individual particles of air whose vibration produces the sound were to rush onwards at that rate, every sound would be accompanied by a disturbance of the air amounting to a hurricane.

Thus it is also in the case of light. The motions of the individual particles of the ether take place through immeasurably small spaces, but are communicated with immense rapidity to the next; from these to those beyond them, and so on, even through the vast distances between the heavenly bodies. So long as the ether through which the light-wave travels is of uniform density—as we must suppose it to be in free space, and in media of uniform constitution, such as water, glass, and other uncrystallised bodies—the wave spreads with equal velocity in all directions; consequently, all the particles to which the motion extends at the same instant are situated on the surface of a sphere having the luminous body in its centre, and the illumination extends in lines at right angles to this wave-surface, that is to say, in straight lines radiating from the luminous body: these lines are called rays of light. When any change of density takes place in the medium, the wave-surface is no longer perfectly spherical, and the rays are broken or curved according as the change of density is sudden or gradual.

The vibrations of the particles of an elastic medium may be of two kinds: 1. *Direct* or *longitudinal*, when the line of vibration coincides with, or is parallel to, the direction in which the wave travels onwards, as in the case of sound-waves in air.—2. *Transverse* or *normal*, when the particles vibrate in directions at right angles to the motion of the wave, as is the case with waves in water, and with the vibrations of a stretched cord set in motion by drawing a bow across it.

Suppose a particle of an elastic medium to be disturbed in any direction whatever. This direction will in general be oblique to the line joining this particle with the next, and the actual velocity of the particle may be resolved into three others, one in the direction of the line of junction between the two particles, that is to say, in the direction in which the wave-motion proceeds, the other two in a plane at right angles to it. The first component determines the longitudinal, the other two the lateral motion or vibration of the particle; and the relative distances to which these two kinds of vibration are propagated depends upon the peculiar constitution of the medium. When the air is set in motion by the vibrations of a sounding body, it is the longitudinal vibrations which travel onwards, producing a series of compressions and dilatations of the air along the line of the wave, and these motions ultimately reaching the ear, produce the effect of sound: the lateral vibrations, on the other hand, appear to be quickly extinguished; at all events, they produce no effect upon the ear. With the vibrations of the luminiferous ether, however, the case is exactly reversed; for, as will be seen hereafter, the phenomena of polarised light show plainly that the transverse vibrations of the ether are the only ones which affect our visual organs. With regard to many phenomena, however, the particular directions of the vibrating particles may be left out of consideration.

To explain more clearly the mode of transmission of the transverse vibrations of the ether-molecules, suppose that a row of these particles, *a*, *b*, *c*, *d* (*fig.* 640), situated in a homogeneous medium, is brought by any disturbing force into the position *a′ b′ c′ d′*. The sum of the forces which hold the particles *m*, *n*, of the contiguous rows in their places will then be altered. If the displacement itself is small in comparison with the distances between the molecules, the forces at right angles to the line of displacement will remain unaltered; but the repulsion exerted by *b* upon *n* in the direction of displacement has increased, while that of *d* upon *n* is diminished. The same is true with respect to *m*, and all the particles in the same horizontal row, which, therefore, soon move in the same direction as *a*, *b*, *c*, *d*. This latter row of particles is, however, urged back to its original position, with a force equal to that with which it set the other particles in motion; so that its velocity in the primary direction is gradually destroyed, and it returns to its original position, which, however, it passes beyond, in consequence of the momentum which it has acquired, thus performing a succession of small oscillations like those of a pendulum. Similar oscillations are performed successively by the second, third, and other rows of particles; and if by the time that the first row of particles, *a a′* (*fig.* 641), has completed a single oscillation, backwards and forwards, the vibratory motion has extended as far as *b*, the rows of particles between *a a′* and *b b′* inclusive will exhibit all possible phases of the movement. The distance *a b* between two layers of corresponding phase is the length of a complete wave; the ray *r s*, or the wave-surface normal to it, traverses this distance in the time in which the row of particles *a a′* performs a complete oscillation. The greatest distance attained by any particle from its position of equilibrium during the time of a complete oscillation, is called the amplitude of the vibration. It is proportional to the greatest velocity of the particle during its passage through its position of equilibrium. The intensity of the light is proportional to the *vis viva* of the vibratory particles, and therefore to the square of the amplitude of the vibration.

Fig. 640.

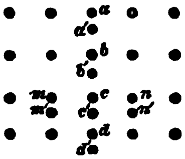
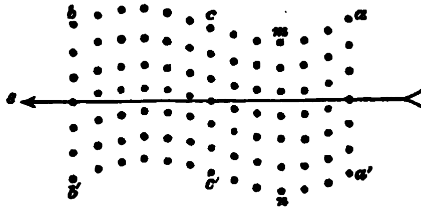


Fig. 641.



Velocity of Light. The rate at which a wave travels through an elastic medium is a function of its elasticity and density, and when these are known, as in the case of sound, the rate of propagation may be calculated *a priori*, by the formula $v = \sqrt{\frac{e}{d}}$ (see p. 41). But, in the case of light, these elements are unknown, and therefore the velocity can only be determined by observation. The following methods have been adopted:—

1. By *Observations of the Eclipses of Jupiter's Satellites.*—This method was proposed and carried out by the Danish astronomer Römer in 1676. He found that, when the earth is between the sun and Jupiter, that is to say, at its least distance from that planet, the nearest of Jupiter's four moons enters the shadow of the planet at intervals of 42 h. 28′ 35″. Now, calculating from this the time at which the 100th eclipse should take place, observation showed a retardation of 15 minutes behind the calculated time. But in the same interval, the earth had travelled about half round its orbit, and had therefore increased its distance from Jupiter by nearly half the diameter of that orbit. This then was the distance which the light from Jupiter had passed over in 15 minutes; and thence the velocity of light was found to be 77,000 leagues, or 167,600 geographical miles per second. At this rate it takes 8′ 13″ to reach us from the sun, 4h. 10′ from Neptune, and about 10 years from the nearest fixed star (61 *Cygni*).

2. By *the Aberration of the Fixed Stars.*—The motion of the earth in its orbit, combined with that of the light coming from the stars, causes them to appear, not in their

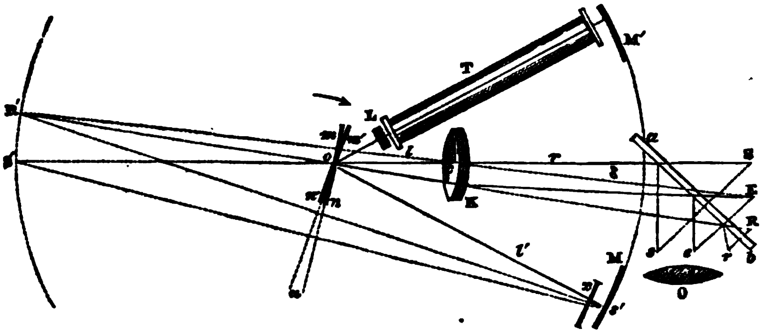
true places, but in the direction of the resultant of these two motions. The apparent positions of all the stars are, accordingly, shifted in the direction in which the earth is moving. Each star, in the course of the earth's annual revolution, describes a small ellipse round its true place; for a star in the pole of the ecliptic, this ellipse is nearly a circle of 20·445″ apparent diameter. The tangent of this angle gives the ratio between the velocity of light and that of the earth in its orbit; and the latter being known by independent observation, the velocity of light is thence found to be 166,072 geographical miles per second, a result differing from that of Römer by less than 1 per cent. It must also be observed that Römer's method gives the velocity of reflected light in free space, whereas the aberration method gives the velocity of direct light in air.

3. *Measurement of the velocity of light by small distances.—a. Fizeau's method.* A toothed wheel having its teeth of the same width as the intervals between them is made to revolve rapidly, so that its teeth may pass through a beam of light proceeding from a lamp or other source, the light being thus intercepted by the teeth, and passing through only at intervals. The light which passes between the teeth of the wheel is reflected perpendicularly from a plane mirror placed at a great distance; it then returns along the same path, and again passes between the teeth of the wheel. Now, during the time occupied by the light in travelling twice over the space between the wheel and the mirror, the wheel will have performed a certain part of its revolution; and if it turns with a due degree of velocity, the light which has passed in the first instance between two of the teeth will strike, at its return, on the face of a tooth instead of a space between two teeth, so that an observer looking through the wheel in the direction of the mirror, will not, in that case, perceive any light. The time which the light takes to pass from the wheel to the mirror and return, is therefore equal to that in which a tooth of the wheel moves into the place previously occupied by the space immediately preceding it, which time is easily calculated from the known velocity of the wheel and the number of its teeth. If, for example, the wheel has n teeth and makes t revolutions per second, each tooth will pass into the place of the preceding tooth in $\frac{1}{nt}$ of a second, and into the place of the space next preceding, in $\frac{1}{2nt}$ of a second. Fizeau's experiments, in which the wheel and mirror were placed at a distance of 8633 metres (between Turesnes and Montmartre), gave, as the velocity of light in air, 78,841 leagues of 4 kilometres each per second. Römer's method gave 77,000 leagues.

Fizeau's method might be applied to show that rays of light of all colours (like waves of sound of every pitch) travel with the same velocity. This conclusion may, however, be regarded as established by the fact that all the stars, whatever may be their colour, exhibit equal aberration, which could not be the case if rays of different colour travelled with different velocities.

β. By means of a Revolving Mirror.—This method, proposed by Arago, and carried out independently by Foucault, and by Fizeau and Breguet, is similar in principle to that by which Wheatstone determined the velocity of electricity, and affords the means of measuring the velocity of light in a space not exceeding four metres. A line of light, S (*fig.* 642), proceeding from a very narrow rectangular aperture at right angles to the plane of the figure, after passing through the converging achromatic lens K, which would form an image of it at S′, falls upon a plane mirror, *mn*, capable of revolving on a vertical axis passing through *o* on the line S S′, which reflects it to *s′*, a point symmetrical with S′, as regards the mirror. At this point is placed a concave spherical mirror, M, whose

Fig. 642.



centre of figure is in *o*. The light falling on this mirror is reflected back again along the same path, *s'o*, to the plane mirror, *mn*, which again reflects it to S in a beam coinciding with the incident light. This will be the case in all positions of the mirror *mn*, provided the light is reflected from it to M. As the image thus sent back to S would be confounded with the incident beam, an unsilvered plate of glass, *ab*, is placed in such a position, that the light falling upon it in the direction *o*S may be partly reflected to *s*, where it may be observed by an eye-piece furnished with a vertical wire. If the mirror *mn* be made to revolve slowly, an eye placed at *s* will see the image of the line of light at intervals, but if the mirror makes more than 10 turns in a second, the image will be seen continuously; and if the eye-piece be adjusted, so that the image shall coincide with the wire, when the mirror makes from 20 to 30 revolutions per second, it will be seen to deviate in the direction of the rotation when the rate is increased to several hundred turns per second; if, for example, the mirror turns in the direction of the arrow, the image will be displaced from S to R, or from *s* to *r*. The cause of the displacement is that the mirror *mn* has time to revolve through a sensible angle, during the time occupied by the light in travelling from *o* to *s'* and from *s'* to *o*, so that the beam of light, at its second reflection from *mn*, is deflected from its first direction, forming, with the incident beam S*o*, an angle equal to twice the angular displacement of the mirror.

The mode of calculating the velocity of light from the observed deviation is as follows:—Let S*c* = r; $co = l$; $os' = l'$; the arc of deviation SR or $sr = d$; also let n be the number of turns performed by the mirror *mn* in a second, and V the velocity of the light. The mirror *mn* having moved into the position *m'n'*, by the time that the ray reflected from M returns to it, the deviation would be equal to the angle S*o*R, if the ray were not deflected by the lens *c*K, or, which comes to the same thing, if the point *c* coincided with *o*. Suppose, first, that this is the case; then the angle S*o*R is equal to twice the angle a, through which the mirror revolves during the time occupied by the light in passing over the space $2os' = 2l'$. This time is $\frac{2l'}{V}$, and since the mirror makes n turns in a second, the angle $a = \frac{2nl}{V}$. The angle of deflection of the ray is therefore $\frac{4nl'}{V}$, and the corresponding arc, whose radius is $o\mathrm{S} = r + l$, is

$$d = 2a \, . \, 2\pi \, . \, \overline{o\mathrm{S}} = \frac{8\pi nl'(r+l)}{V}.$$

But the reflected ray is actually deflected by the lens K. Draw R'*c* through the optic centre *c* and the point R', which is the image of *s'* in the mirror *m'n'*. The image of R', formed by the lens K, will then be at E, and the angle of deviation will be S*c*E = δ. Now the triangles *o*R'S', *c*R'S', give $\sin \mathrm{R'}c\mathrm{S'} = \sin \delta = \frac{\mathrm{R'S'}}{\mathrm{S'}c} = \frac{\mathrm{R'S'}}{l+l'}$; and $\sin \mathrm{R'}o\mathrm{S'} = \sin 2a = \frac{\mathrm{R'S'}}{l'}$. Hence, replacing the angles (which are very small) by their sines, and substituting for $2a$ its value $\frac{4nl'}{V}$, we find $\delta = \frac{4nl'^2}{V(l+l')}$; and for the arc SE = $D = 2\pi r\delta$:

$$D = \frac{8\pi l'^2 nr}{V(l+l')}; \text{ whence } V = \frac{8\pi l'^2 nr}{D(l+l')},$$

a formula which gives the velocity of light as a function of the deviation.

The same method serves also to measure the velocity of light in water or any other liquid, a tube T containing the liquid, and closed at the ends with flat glass plates, being interposed between the mirror *mn* and M'. As, however, the light would be refracted by the liquid, and therefore the focus would not fall on M', a diverging lens is placed at L to compensate for the deviation thence arising.

Moreover, as the column of water does not occupy the entire space between the mirrors, the velocity calculated as above from the observed deviation is only the mean velocity of light in a space occupied partly by water and partly by air. Let U be this mean velocity; w and a the spaces occupied by the water and air respectively; V' and V the corresponding real velocities. The times occupied by the light in traversing the spaces a and w are $\frac{a}{V}$ and $\frac{w}{V'}$, and the whole time is $\frac{aV' + wV}{VV'}$. Hence, dividing the total space $a + w$ by the time, we find for the mean velocity:

$$U = \frac{VV'(a+w)}{aV' + wV},$$

whence

$$V' = \frac{wUV}{(a+w)V - aU}.$$

By this method it is found that the velocity of light in water is less than in air, a result which, as will be seen hereafter, is in accordance with the wave-theory, while it is directly opposed to that which would follow from the theory of emission.

Intensity of Light. The intensity of the light received by a surface from any given source—that is to say, the quantity of light received by a unit of the surface—depends partly on its distance from that source, partly on the obliquity at which the light falls upon it.

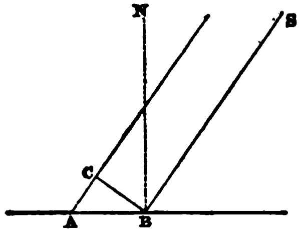
1. *The intensity of light emanating from a point varies inversely as the square of the distance.* For, as the undulations excited by the luminous source travel with equal velocity in all directions—supposing the medium uniform—they may be regarded as spreading out in concentric spherical surfaces of continually increasing magnitude; and as these surfaces are to one another as the squares of their radii, it follows that the quantity of light received by a unit of surface will vary inversely as the square of the radius of the sphere of which it forms a part—that is to say, as the square of its distance from the luminous point.

If the luminous body is of finite dimensions, the preceding law, being applicable to the light emanating from each point of its surface, must likewise hold good with regard to the whole, provided the body is sufficiently distant to admit of all its points being regarded as equally distant from the illumined surface; and since the apparent diameter varies inversely as the distance, *the intensity of the light will vary in direct proportion to the square of the apparent diameter* or to the *apparent surface* of the luminous body, understanding by this last term the conical angle of a cone enveloping the body and having its vertex at the luminous point.

2. *The intensity of the light received by any surface varies as the cosine of the angle which the incident rays make with the normal to that surface.* For suppose A B (*fig.* 643) to be a portion of the illuminated surface, so small that the rays falling upon it may be regarded as parallel. The quantity of light received by A B, is the same as that which would fall on its projection B C, on a plane perpendicular to the direction of the rays, and therefore exposed to their full effect; hence the intensity of the light falling on these two surfaces is inversely as their areas; but $BC = AB . \cos ABC = AB . \cos SBN$, the angle which the incident rays make with the normal B N.

3. *The intensity of the light emanating from a self-luminous surface, is proportional to the cosine of the angle which the rays make with the normal.* This proportion may be demonstrated in a similar manner to the preceding, and the result may be verified by looking through a small aperture at an incandescent surface, as that of red-hot iron, and inclining it more and more to the direction of the rays proceeding from it to the eye. In accordance with this law, it is found that the brightness of a luminous surface is independent of its form and of its position with regard to the visual rays, the impression produced by it on the eye being the same as that produced by a plane surface of equal intrinsic lustre, which is the projection of the original surface on a plane perpendicular to the visual rays: a red-hot ball, for example, seen from a distance looks just like a flat disc.

Fig. 643.



Comparison of the Intensity of two Luminous Sources: PHOTOMETRY.

The eye is not capable of judging directly, with any great approach to accuracy, of the relative intensity of two lights, but it can perceive with great nicety whether two contiguous surfaces or portions of the same surface are equally illuminated, or whether two contiguous shadows have or have not the same depth. On this principle are constructed most of the instruments called *Photometers*, for measuring the relative intensity of different sources of light.

Rumford's *Photometer*, which is very easily constructed, consists of a small wooden cylinder set upright in front of a sheet of white paper, also placed vertically. The two lights to be compared (a candle and gas-flame, for example) are placed at the same height in front of the paper, and in such a manner that the two shadows of the wooden cylinder which they cast, shall fall on the paper close together, and that the rays from both of them shall meet the paper at the same angle. Each shadow will then be illuminated by only one of the lights, while the rest of the surface will receive the rays from both, and the two shadows will be of the same depth when the surface of the paper is equally illuminated by both lights. If then the stronger light be moved farther off till the shadows are equally dark, the intensities of the two will be directly as the squares of their distances from the screen when that condition is fulfilled.

This photometer gives very exact results in many cases; but in applying it to determine the relative illuminating power of a gas-flame and a candle, a difficulty arises from the different colours of the two shadows, that of the gas being bluish-brown, while that of the candle is yellowish-brown. In all such cases, Bunsen's photometer, whose indications do not depend on depth of shadow, is much more convenient.

Bunsen's *Photometer* consists of a screen of thin writing paper stretched on a frame, and saturated with a solution of spermaceti in oil of turpentine, except a spot in the centre about the size of a shilling. A light of constant intensity being placed at a fixed distance behind the screen, the ungreased spot appears darker than the rest of the screen. One of the lights to be compared is then placed in front of the screen, so that its reflected rays may be added to the light transmitted from behind, and adjusted so that the ungreased spot shall be illuminated just as much as the rest of the surface, and shall therefore be no longer visible. This will be the case when $T + r = t + R$, denoting by T, t, the quantities of light transmitted by the uncovered part of the screen, and the part covered by the disc respectively, and by R, r, the quantities reflected. A precisely similar experiment being then made with the other source of light, the intensities of the two will be to one another as the squares of their distance from the screen at which the disappearance of the disc takes place. Sometimes the grease is applied only to a small circular spot in the centre of the screen, which then transmits more light than the rest of the surface.

Masson's *Electro-photometer*. This apparatus has the advantage of admitting of the comparison of lights of different colours. It consists of a circular disc divided into white and black sectors of equal size, and set in motion by clock-work at a uniform rate of 250 to 300 revolutions in a second. If it be then illuminated by a constant source of light, such as a lamp, it appears of a uniform grey tint, in consequence of the duration of the visual impression on the eye. But if it be illuminated by an instantaneous light, such as the electric spark, the black and white sectors become distinctly visible, and appear as if they were fixed, because they have not time to move through a sensible angle during the extremely short interval for which the spark continues. If now the intensity of the light afforded by the spark be gradually diminished, as by removing it to a greater distance, the source of constant light still remaining, the increase of illumination which the spark affords to the disc ultimately becomes too feeble to render the sectors visible, so that the disc still continues to exhibit a uniform grey tint. The relative intensities of the constant and instantaneous lights at which this limit is attained, evidently depend upon the number of the sectors and the velocity of revolution.

The relative intensities of two electric sparks are as the squares of the distances to which they must be removed from the disc to cause the sectors to disappear, while the disc is illuminated by a constant light. On the other hand, to use the instrument for comparing the intensities of two continuous lights, a succession of electric sparks is made to pass in front of the disc, and one of the constant lights is made to approach it till the sectors cease to be distinguishable. The same experiment being then made with the other light, the intensities of the two are as the squares of the distances thus determined.

By means of this instrument, M. Masson has demonstrated the following laws relating to the intensity of the electric light. 1. *It is proportional to the coated surfaces by the discharge of which, at a constant distance, the spark is produced.* 2. *It is inversely as the distance between those surfaces, or as the thickness of the jar.* 3. *It is proportional to the square of the striking distance.* 4. *The quantities of light in the spark are proportional to the quantities of heat developed in a wire forming part of the same circuit.*

General results of photometric observation.—1. By comparing the quantities of light emitted by the same number of flames in different relative positions, it is found that flame is perfectly transparent; in fact the luminous effect of a series of candles placed side by side, is the same whether they are arranged in a line perpendicular or parallel to the direction of the rays. In like manner, a flat gas-flame, like that of a bat's-wing burner, gives the same amount of light in all directions.

2. It appears from observations by Bouguer, made with Rumford's photometer, that one of the shadows thrown by lights of equal brightness disappears when one of these lights is placed 8 times as far from the screen as the other—that is to say, when the nearer light illuminates the screen 64 times as strongly as the other. Hence it appears that light emanating from any source becomes imperceptible in presence of another 64 times as strong; the disappearance of the stars in daylight shows, therefore, that the diffused light of the earth's atmosphere must be at least 64 times as strong as that sent to us from any of the stars.

3. When the flames of two lamps or candles touch one another, the intensity of the

combined flame is greater than the sum of the intensities of the separate flames. This effect, first observed by Franklin, appears to be due to the increased temperature at the part where the flames overlap. Rumford found that a number of flat cotton wicks impregnated with oil, gave a much greater amount of light when they were placed together nearly in contact, than when they were separated. On the same principle, Arago and Fresnel have constructed lamps for light-houses, in which a number of concentric wicks are arranged with small spaces between them, through which a current of air is made to pass by the draught of a chimney. The flame being transparent, a considerable amount of light is thus obtained within a small space.

4. The photometric method serves also to determine the illuminating equivalents of different light-giving materials. Rumford found that 100 pounds of wax burnt in the form of a taper, were equal in light-giving power to 101 lbs. of tallow, if the candles were well snuffed, and 229 lbs. if the wicks were allowed to grow long; to 100 lbs. of olive oil burnt in an Argand lamp, and 129 in a lamp burning without smoke; also to 125 lbs. of rape oil, and 120 lbs. of linseed oil in a common lamp. Péclet calculated the following table of the expense per hour of various modes of illumination, yielding a quantity of light equal to that afforded by a gas-jet burning at the rate of 5 centimes per hour:

	Centimes.		Centimes.
Carcel lamp	5·8	Wax taper of 100 grm.	48·6
Candle of 82 grm.	9·8	Stearine candle	18
Candle of 10 grm.	12·0		

It appears from this comparison that gas is the most economical of all illuminating materials. The results depend, however, in a great measure on the facility of access of air to the flame, the form of the wick or burner, and the length of the flame. For numerous determinations of the illuminating equivalents of various kinds of gas, and other light-giving substances, see *Ure's Dict. of Arts, &c.*, articles Coal-gas (i. 734) and Illumination (ii. 493).

Interference.

When two or more waves pass over the same part of a medium, each of them affects the particles of the medium disturbed by the other just as it would have affected the same particles in a state of rest. Consequently, the state of any particle affected by the two waves at once, will be the same as that which would have resulted if it had been first disturbed by the one wave, and then the second had acted upon it while in that disturbed state. Thus the height of the tide is found by calculating the heights to which it would be raised by the sun and by the moon acting separately, and taking the sum or difference as the case may be.

Suppose now two waves of equal breadth and intensity (equal height in the case of water) to proceed from the same, or nearly the same point, and travel onwards one after the other; then, if they meet in such a manner that the phases or alternations of the one coincide with the phases or alternations of the other, the result will be a compound wave, having the sum of the intensities of the separate waves; this will be the case if the paths along which they travel before meeting are of equal length, or if one exceeds the other by any exact number of whole undulations, as in *fig.* 644; but if the phases of the one are exactly opposed to the phases of the other, which is the case when the one wave is behind the other by any odd number of half-undulations, as in *fig.* 645, a wave will be produced whose intensity equals the difference of the intensities of the separate waves, and if these are equal, the vibratory motion will be completely destroyed and the particles of the medium brought to rest along the whole line of the combined waves. If the paths of the two waves do not differ by any exact number of half undulations, even or odd, the result will be intermediate between the two just considered, the intensity of the combined wave being always less than the sum and

Fig. 644.

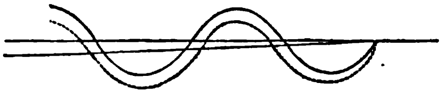
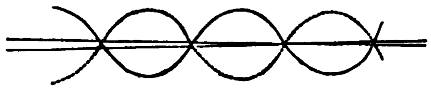


Fig. 645.

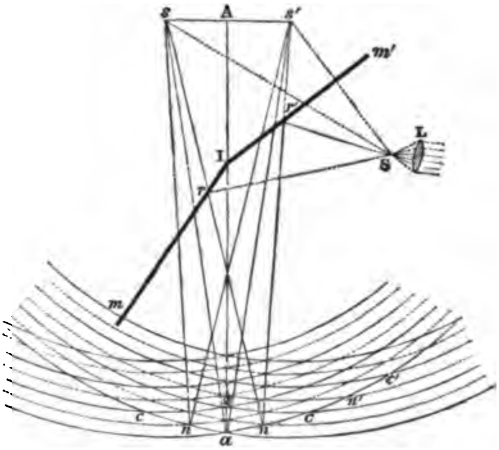


greater than the difference of the separate waves. This composition or superposition of oscillations is called Interference. In order that it may take place along a whole line of wave, it is clear that the component waves must be of the same breadth, and that they must proceed from points very near each other, otherwise their paths will intersect only at isolated points.

Let us now enquire whether these principles are applicable in the case of light. If light consists of undulations, and these undulations are governed by ordinary mechanical laws, it must follow that two rays of light may meet one another in such a manner as to counteract each other's action and produce darkness; and such, in fact, is found to be the case.

Suppose *s*, *s′* (*fig.* 646) to be two radiant points very close together, and producing in the luminiferous ether, waves of the same length (of red light, for example) and always in the same phase of vibration at the instant of starting from these points. Imagine also two series of spherical wave-surfaces having the points *s*, *s′* for centres, and with radii increasing successively by half the length of a wave $= \frac{\lambda}{2}$. These surfaces will cut the plane of the figure in two systems of arcs, which will intersect one another in the manner shown in the figure, in which each two consecutive arcs, one represented by a full, the other by a dotted line, are separated by the interval $\frac{\lambda}{2}$, and each pair of alternate arcs (both full or both dotted) by the interval λ, or a whole undulation.

Fig. 646.



Consider now the point *a*, situated on the line A*a*, drawn perpendicular to *ss′*, through its middle point A. The two rays *sa*, *s′a*, being of equal length, are in the same phase of vibration: consequently their intensities will be added to one another and will produce increased light, and the same effect will be produced at *c*, *c′*, and at all the intersections of the continuous arcs, where the difference in length of the rays proceeding from the points *s*, *s′* is equal to any multiple of λ or to any even multiple of $\frac{\lambda}{2}$. But at *n*, *n′* or any other intersections of a continuous and a dotted arc, where the difference in length of the rays *sn*, *s′n*, &c., is equal to $\frac{\lambda}{2}$, or any odd multiple thereof, the rays are in opposite phases, so that their vibrations act against one another, and the amount of light at those points is less than it would be if only one of the rays arrived there. The distance between the points *s*, *s′* being very small compared with A*a*, the surface *anc* is very nearly plane, so, that if a white screen be placed there, a succession of luminous points, *a*, *c*, *c′*, &c., will be formed upon it separated by dark spaces, *n*, *n′*, &c.

If the sources *s*, *s′*, instead of being luminous points, are lines of light perpendicular to the plane of the figure, a series of alternate light and dark bands, or fringes, will be produced parallel to those lines.

The conditions essential for exhibiting these effects are, that the two luminous sources *s*, *s′* shall be very near one another, and that the waves emanating from them shall always be simultaneously in the same phase. These conditions are most easily fulfilled by the following arrangement devised by Fresnel:—

A beam of light entering through a rectangular slit in the shutter of a darkened room, and passing through a plate of red glass, is condensed at S to a very fine line of light, by a cylindrical lens L (*fig.* 646) of very short focus. The rays there cross each other, and fall upon two plane mirrors I*m*, I*m′*, placed together at a very obtuse angle, and having their line of intersection parallel to the line of light. The rays, after reflection from these mirrors, proceed as if they had originally issued from two points *s*, *s′*, situated symmetrically to the point S, behind each of the mirrors. The mirrors being placed nearly in one plane, the points s s' are very close together, so that all the conditions are fulfilled for the production of light and dark fringes on the screen, as above described.

Instead of reflecting the light diverging from S from two plane mirrors, it may be made to pass through a glass prism having a very large refracting angle. The fringes also, instead of being received on a screen, may be viewed through a telescope, and their angular breadths estimated by micrometrical measurement.

If the beam of light proceeding from one of the points s, s', be intercepted, the whole of the fringes disappear, and the light from the other source produces a uniform illumination on the screen, plainly showing that the fringes are produced by the combination or interference of the rays proceeding from the two sources.

Measurement of the lengths of the waves of light.—The breadths of the fringes having been ascertained, as above described, an easy calculation gives the lengths of the waves of the particular light by which they are produced. In *fig.* 646, the length of the wave λ is equal to the distance sa. Now the curvilinear triangle asc may be regarded as a right-angled triangle, whose hypothenuse $ac = b$ is the distance from the centre to the first bright lateral fringe. Moreover, the angles sca and $sas' = \omega$ are equal, because their sides are respectively perpendicular to one another: hence

$$\lambda = b \sin \omega.$$

Hence to obtain the value of λ, it is sufficient to measure the angle sas' with a repeating circle, and the distance ac with a micrometer. A more exact mode of determination will be described hereafter.

The length λ is proportional to the distance ac. Now the breadth of the fringes is found to be greatest in red and least in violet light, and of intermediate breadths for the intermediate colours of the spectrum: hence also it follows that *the lengths of the waves are greatest in red and least in violet light.*

The formula $\lambda = \frac{v}{n}$, in which v is the velocity of light, and n the number of vibrations per second, shows that the vibrations are most rapid in violet, and least rapid in red light.

The length of the wave and the rapidity of vibration of the particles of the ether determine the colour of the light, just as the length of the sound-wave and the rate of vibrations of the particles of the air, determine the pitch of sound.

The following table exhibits the wave-lengths and the number of vibrations per second of the mean rays of the several colours of the spectrum, and of the principal fixed lines:

Fixed lines and colours.	Values of λ in ten-thousandths of a millimetre.	Number of vibrations per second in millions of millions.	Fixed lines and colours.	Values of λ in ten-thousandths of a millimetre.	Number of vibrations per second in millions of millions.
Line B . .	6·88	. .	Mean green .	5·12	601
Line C . .	6·56	. .	Line F . .	4·84	
Mean red .	6·20	497	Mean blue .	4·75	648
Line D . .	5·89	. .	Mean indigo .	4·49	686
Mean orange .	5·83	528	Line G . .	4·29	
Mean yellow .	5·51	529	Mean violet .	4·23	728
Line E . .	5·26	. .	Line H . .	3·93	

The expression $b = \frac{\lambda}{\sin \omega}$, which gives the breadth of the fringes in terms of the wave-length and the angle ω, shows that for each colour they are broader in proportion as that angle is smaller. If it is too large, that is, if the distance s s' is too great in proportion to A a, the fringes disappear altogether; they are still visible, however, when this angle has a magnitude of several degrees.

The fringes being of different breadths in the different coloured lights, and white light, as will hereafter be shown, being a mixture of all the colours of the spectrum, it follows that when the preceding experiment is made with white light (sun-light, the electric light, or the lime-light), the bands produced are not simply bright and dark alternately, but exhibit a succession of colours produced by the combination of the simple colours in various proportions, and not separated by any absolutely dark bands. Moreover, these coloured fringes are much less numerous than the simple light and dark bands produced by homogeneous light, because the breadths of the simple-coloured fringes of which they are composed do not vary proportionally to one another, as their distance from the centre increases; hence, they ultimately become mixed, and reproduce white light. Even the simple fringes formed in homogeneous light become less and less distinct as they recede from the centre, and ultimately disappear when the difference between the lengths of the rays which form them becomes equal to a certain number of half-undulations. The cause of this disappearance is, that the light used in the experiment is never absolutely homogeneous, and that the want of perfect equality between the lengths of the waves which compose it, ultimately makes itself perceptible, the fringes of different breadths overlapping and effacing each other in the same manner as when white light is used, though at a much greater distance from the centre. Whatever kind of light is employed, the fringes are more distinct and numerous in proportion as the line of light is narrower, provided it be wide enough to give the required amount of illumination; for it is evident that a broad aperture may be regarded as a number of narrow ones placed side by side, each producing its own set of fringes, which, as they do not coincide in position, will overlap and efface each other more or less completely.

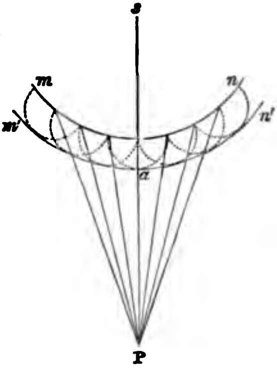
If a very thin plate of glass, mica, selenite, or other transparent substance be placed in front of one of the mirrors (*fig.* 646), so that the rays proceeding from one of the points, *s*, *s'*, shall be obliged to pass through it before reaching the screen or telescope, the whole of the fringes will be displaced towards the side on which the transparent plate is situated, so that the central fringe *a* will no longer be opposite to A. Suppose the displacement to be towards the right of the figure; then the line *s'a* will be shorter than *sa*. Now, as the two rays forming this central fringe must contain the same number of wave-lengths, it follows that these wave-lengths are less in the more highly refracting substance (glass, &c.) than in the air. The velocity of the light is, therefore, diminished in the more highly refracting medium; and experiment shows that the retardation thus produced is greater as the refracting power is greater. This result is in accordance with the direct measurement of the velocity of light in air and water (p. 595), and likewise, as we shall presently see, with the law of refraction. Moreover, as the velocity of transmission of vibrations in an elastic medium is related to its elasticity and density by the equation $v^2 = \frac{e}{d}$, it follows also that the elasticity of the ether is least, or its density greatest, in the most highly refracting media.

The transparent plate used in the experiment just described must be extremely thin; otherwise the fringes will disappear altogether, just as if an opaque screen had been interposed. A thicker plate would, in fact, shift the fringes beyond the space in which the two systems of waves meet each other, namely, the space bounded by the two straight lines passing through *s*, *s'* and the intersection, I, of the mirrors.

Diffraction. The principle of interference serves to explain some very remarkable and beautiful phenomena which are observed when light passes by the edge of an opaque body, or through a small aperture. The effects thus produced consist in this, that the light bends to a certain extent within the geometric shadow bounded by straight lines drawn from the luminous point through the edges of the opaque body, just as a wave in water will turn the angle of a wall, or spread itself through a hole in any fixed obstacle. The result is the formation of a number of alternate bright and dark bands or coloured fringes, sometimes within the shadow, sometimes beyond it, sometimes in both places at once. These effects, formerly known as Inflection, but now called Diffraction, admit of complete explanation on the wave-theory of light, but are quite inexplicable on the theory of emission.

The explanation of diffraction on the undulatory theory depends upon the general principle first enunciated by Huyghens, that—*The vibrations of a wave of light, at each of its points, may be regarded as the resultant of the elementary movements which would be communicated to it, at the same instant, by all the parts of the same wave in any one of its previous positions.* For it is evident, from the elasticity of the ether, and the facility with which vibratory movements are transmitted through it, that its particles do not vibrate independently of each other, but that each may be regarded as a centre of disturbance with regard to all around it. Consequently, each point of a spherical wave, *mn* (*fig.* 647), will produce by its vibration, a number of secondary spherical waves, which, spreading out with the same rapidity, will have for their enveloping surface—that is to say, for the general surface of the wave as it spreads outwards—another spherical surface, *m'n'*, concentric with the former. Hence the vibration imparted to any point P, by the wave *mn*,

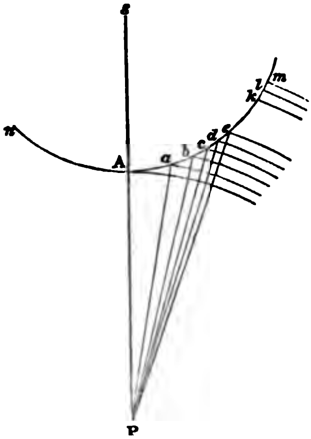
Fig. 647.



when it reaches that point, may be regarded as the resultant of all the secondary disturbances emanating from the several points of *mn*.

To determine the manner in which the movement of P is affected by the several points of the wave in any of its previous positions, draw *s*P, cutting the wave *mn* in A (*fig.* 648), and designating the distance AP by γ, describe, from P as a centre, and with the radii γ, $\gamma + \frac{1}{2}\lambda$, $\gamma + 2 . \frac{1}{2}\lambda$, $\gamma + 3 . \frac{1}{2}\lambda$, &c., a number of arcs cutting the wave in the points *a*, *b*, *c*, *d*, . . . and draw the straight lines P*a*, P*b*, P*c*, &c., which evidently differ from another by half a wave-length. Then it will be found that the intervals A*a*, *ab*, &c. are not equal, but continually diminish from A towards *m*. Further, for every point in *ab*, there exists a point in A*a*, such that the lines drawn from these points to P differ by $\frac{1}{2}\lambda$, and consequently the waves emanating from these points to P will be in complete discordance. Hence, if A*a* were equal to *ab*, its effect on P would be completely neutralised by *ab*; but this not being the case, *ab* can only neutralise part of A*a*, and there remains a portion of the arc A*a*, which produces a certain degree of illumination at P. There is a further reason why *ab* neutralises only part of A*a*, and that is, that it acts more obliquely. Similarly, *cd* will neutralise a part, but only a part, of the action of *bc*. Hence, it will be seen that the illumination produced at P by the half-wave A*m* is the sum of the effects of the arcs of uneven order over those of even order, counting from A. In all cases, however, it is only necessary to take account of that part of the wave which is very near to the line *s*P: for at a greater distance, as at *m*, the arcs *kl*, *lm* become very nearly equal, and, moreover, their action on P is very oblique—for both of which reasons their effect on P may be neglected. The arc A*n* acts exactly like A*m*, so that if the illumination produced by A*m* be denoted by 1, that of the entire wave *mn* will be equal to 2.

Fig. 648.



The arcs A*a*, *ab*, &c. are called **elements of interference**, and the point A is called the **pole** of the point P.

The direction of vibration of the ether-molecule P at any instant is determined by that of the first element A*a*, of the half-wave A*m*; and if this portion were intercepted, the point P would then vibrate in the direction determined by the movement of *ab*, which is opposite to that of A*a*. Hence, it appears that the action of A*a* on P is greater than the resultant actions of all the remaining elements, *ab*, *bc*, &c.: for the motion of P changes its direction according as the element A*a* acts upon it or not. The same is true with regard to each of the elements *ab*, *bc*, &c., the action of each one of them on P being greater than the resultant of all beyond it.

Now, suppose part of the half-wave A*m* to be intercepted by the interposition of an opaque screen; then the arc *ab*, which destroyed a great part of the effect of A*a*, is removed, and the point P receives more light than it did before: for the effect of *ab* is greater than that of all the rest of the wave, from *b* outwards, taken together.—Next suppose the screen to terminate at *b*; then, since *ab* destroys the greater part of A*a*, and the rest of the wave is intercepted, P will now receive less light than it would if the screen were not there. In the same manner, it will be found that whenever the screen is so placed as to leave an odd number of elements of the wave free, the point P will be more illuminated than it would be if the screen were not there, and the contrary if an even number are left free.

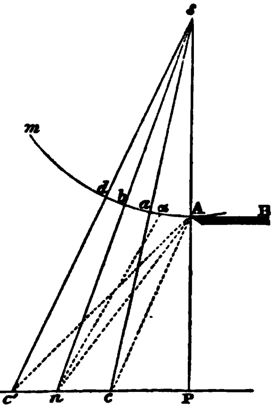
These principles lead immediately to the explanation of the phenomena of diffraction.

1. *Fringes produced by rays passing along the edge of a screen.*—Suppose a beam of homogeneous light proceeding from a luminous point S (*fig.* 649), or better from a fine line of light passing through S at right angles to the plane of the figure, to pass by the opaque screen AB, of indefinite extent towards B, and fall upon another screen CD, covered with white paper. The boundary of the geometrical shadow will be determined by the straight line SAP. The light received at P will proceed from the half-wave A*m*, and may be represented by 1; and from the preceding explanations it follows that the points *c*, *c*′, &c., so situated that $Ac - ac = \frac{1}{2}\lambda$; $Ac' - a'c' = \frac{3}{2}\lambda$, will receive more light than if the screen were not there, and will therefore be the centres of bright fringes; and on the contrary, the points *n* *n*′, &c., for which $An - bn = \lambda$

$An' - b'n' = 2\lambda$, &c., will receive less light than if the screen were away, and will therefore be the centres of dark fringes. The general result may be thus stated: The presence of a screen increases the intensity of the light at every point so situated that the broken line (SA, Ac for example) passing to it from the source of light by the edge of the screen exceeds the straight line (Sc) drawn to it directly from the luminous source, by an *odd* number of half undulations, and diminishes the intensity of the light at every point so situated, that the broken line (SA, An) proceeding to it from the luminous point by the edge of the screen, exceeds the straight line joining it with the luminous point, by an *even* number of half-undulations.

In this manner, a succession of bright and dark fringes are produced beyond the geometrical shadow of AB; they may either be received on the screen CD, or viewed by a telescope directed to the edge A, the latter being of course the better method for exact measurement. They become less and less distinct as their distance from the edge of the shadow increases, because the successive arcs Aa, ab, bd, &c. do not neutralise each other's action completely, so that a small quantity of light always mixes with the dark fringes, increasing in amount as they are more distant from P. Finally, at points situated so far from P that the portion of the half-wave intercepted by the screen is too far from the pole b' to produce a sensible effect, the fringes disappear altogether, and the surface of the screen becomes uniformly illuminated with light of intensity = 2.

Fig. 649.



The fringes are broadest in red, and narrowest in violet light; and in white light fringes of compound colours are formed, as in the experiment with the mirrors.

The locus of each fringe, light or dark, considered at different distances from the luminous source, is a hyperbola, having the points A, s for its foci. The dark fringe n, for example, of the mth order, gives $An - bn = m \cdot \frac{1}{2}\lambda$; and subtracting these equal magnitudes from $sb = sA$, we have $sb - An + bn$, or $sn - An = sA - m \cdot \frac{1}{2}\lambda$. The difference $sn - An$ is therefore constant, whatever may be the length of AP; consequently, the locus of the point n is a hyperbola whose foci are A and S.

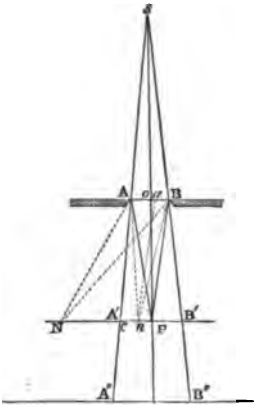
There is also a certain quantity of light *within the geometrical shadow*. For any point p situated to the right of P (*fig.* 649) receives light from a certain portion of the wave Aab; but this portion is smaller and farther from the corresponding pole, as p is more remote from P: hence the brightness of the light diminishes rapidly from the edge of the shadow inwards; but the diminution is continuous and no fringes are produced.

Fringes at the edge of a Mirror.—Rays reflected from the edge of a plane mirror inclined to their direction, proceed as if they had originally issued from a line of light situated symmetrically behind the mirror. The space beyond the mirror may therefore be compared to the opaque screen in the experiment last described: hence the fringes are produced towards the surface of the mirror, whilst a continuous light is visible for a short distance beyond it.

2. *Fringes produced by narrow rectangular apertures.*—Light passing through such an aperture may form fringes in the beam of light itself and in the shadow, separately or together, according to the width of the slit and the distance at which the fringes are viewed. They may be observed by means of a very simple apparatus, consisting of two thin plates of copper fixed in a small frame, one of them being capable of sliding backwards and forwards, so as to vary the width of the aperture at pleasure. On looking at the flame of a candle or other source of light through the slit, brilliant coloured fringes are seen parallel to the edges of the slit. These fringes are also very distinctly seen on viewing the flame of a candle between two fingers held up so as to leave a very narrow space between them.

Internal Fringes.—Let AB (*fig.* 650) be the slit, S the source of light, rendered homogeneous by passing through a coloured glass; and suppose in the first place that the screen A'B', on which the light is thrown, is placed at such a distance that $AP - oP$ and $BP - oP = \frac{1}{2}\lambda$; then all the points of the part AB of the wave-surface will be in accordance with each other, and there will be a bright band at P. The same will be the case *a fortiori*, if the screen A'B' is still farther removed, as to A''B''. But if the screen be moved to a shorter distance from the slit, such that $AP - oP$ is more than $\frac{1}{2}\lambda$, and equal to n times $\frac{1}{2}\lambda$, then if n is even, each half of the wave AB may be divided into an even number of elements of interference, whose actions destroy each other two by two. There will then be a dark band at the central point P. If, on the other hand, n is odd, there will remain one element whose action is not neutralised, and the central band will be bright. Hence, as the screen is gradually removed farther from the aperture, the central band will be alternately bright and dark, until the distance is such that $AP - oP = \frac{1}{2}\lambda$, at and beyond which it will be always bright. The same alternations may be produced by diminishing the width of the aperture AB, while the distance oP remains constant.

Fig. 650.



There are also fringes in the beam of light to the right and left of P. Suppose that the distance of the screen is such that the central band is bright, and $AP - oP = \frac{1}{2}\lambda$, and let n be a point such that $Bn - An = 2 \,.\, \frac{1}{2}\lambda$. The arc AB may then be divided in a, so that $nB - na = na - nA = \frac{1}{2}\lambda$. The vibrations communicated to n by the two arcs An, nB will then destroy one another to a great extent, so that there will be a dark band at n. At c, so situated that $cB - cA = \frac{3}{2}\lambda$, there will be a bright band, because the arc AB may then be divided into three elements of interference, and so on. A precisely similar explanation applies to the case in which the central band is dark.

The interior fringes recede farther from the central point P, as the distance of the screen is greater in proportion to the width of the aperture; and when the screen is placed at such a distance that $BA'' - AA'' = \frac{1}{2}\lambda$, the first dark band will be at A″, and consequently there will be no fringes within the beam of light passing through the aperture; the distance of the screen at which they cease to be produced is less as the aperture is narrower.

External Fringes.—The mode of production of these fringes is similar to that of the internal fringes just considered. Any point N, within the shadow on either side, will be a centre of a dark or a bright band, according as $NB - NA$ is equal to an even or an odd number of times $\frac{1}{2}\lambda$. These external fringes rapidly lose their distinctness as they recede from the edge of the geometric shadow, and disappear altogether when the slit is so wide that the vibrations emitted from the point B are no longer sensible at A. For the simultaneous production of external and internal fringes, therefore, the aperture must be neither too wide nor too narrow.

The loci of both the external and internal fringes are hyperbolas having their foci in A and B. All the fringes are broadest in red and narrowest in violet light, and in white light are made up of bright bands of various colours.

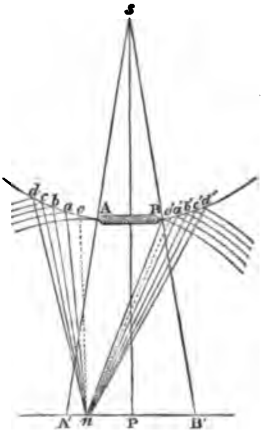
3. *Fringes produced by two narrow slits very close together.*—The two beams of light interfere and produce fringes, precisely as in Fresnel's experiment with the mirrors. This, which is Young's form of the experiment, is similar to that by which Grimaldi originally showed that light added to light may produce darkness.

4. *Fringes produced by very narrow screens.*—In this case also fringes are produced both within and without the shadow. A hair or a thin wire held between the eye and the flame of a candle or a bright line of light, exhibits these fringes very distinctly. Suppose that the screen A B, instead of being of indefinite extent towards B, as in *fig.* 649, is so narrow that the light passing by each of its edges A, B (*fig.* 651), goes beyond the middle of the geometric shadow A′B′; the rays will then act upon each other so as to produce fringes within the shadow, independently of those beyond it. The latter are also modified, because the points at which they are formed likewise receive light from the opposite edge of the narrow screen, which contributes to their formation; in fact, on interposing an opaque body so as to cut off the light from one edge of the screen, the external fringes immediately alter their appearance, and the internal ones disappear altogether.

Formation of the internal fringes.—If the screen AB (*fig.* 651) is not extremely narrow, the internal fringes differ but little from those which would be formed by two slits placed at A and B; for the direction of vibration at any point n within the shadow is then determined by the action of the two elementary portions of the wave immediately contiguous to A and B. When the screen is extremely narrow, the result is the same, excepting that the effect of the first elements of interference Aa, Ba, of the arcs Ad, Bd', being modified by the other portions of these waves, which partly neutralise their action, the points, o, o', from which the resultant actions of these waves may be considered as proceeding, are situated somewhat closer to A and B than they would be if the portions of the wave beyond *a* and *a'* were cut off. At any point *n* within the shadow, there will be a light or a dark band (in homogeneous light), according as *o'n* – *on* is equal to an odd or even number of half-undulations. The point P in the middle of the geometric shadow, being perfectly symmetrical with regard to the arcs A*d*, B*d'*, receives from them accordant impulses, and is therefore the centre of a bright band.

The fringes are wider apart in proportion as AB is smaller, because in order, to obtain a given difference of length in the rays *on*, *on'*, the point *n* must then be taken farther from P. This may be verified by viewing a needle held parallel to a bright line of light; the fringes are then much broader near the point than near the eye.

Fig. 651.



5. *Fringes produced by screens or apertures which are very small in all directions.*—The effects in this case are much more complicated than in those above considered, where the edges of the screen or aperture are supposed to be straight, and so much elongated that it is sufficient to consider the effect of the cylindrical wave situated in a section at right angles to the screen or aperture. But in the case now under consideration it is necessary to consider the actions resulting from all the points of the free surface of the wave, and the problem becomes too complicated to be treated without the aid of the higher analysis. We shall therefore merely enumerate the effects produced in a few of the more simple cases.

When rays proceeding from a luminous point pass through *a small circular aperture* circular fringes are formed, both within and beyond the geometric image. The circular aperture may in fact be regarded as a number of very narrow rectilineal apertures radiating from the centre. In homogeneous light the rings are equidistant, and their diameters are inversely as that of the aperture, excepting that the distance from the centre to the first ring is less than that between two consecutive rings. The centre is bright or dark, according to the proportion between the size of the aperture and its distance from the screen, and either the external or internal rings may disappear according to these dimensions.

A small circular screen also produces fringes similar to those of the linear fringes formed by a narrow rectangular screen. At certain distances, the centre of the shadow is as bright as if the screen were not there.

A small rectangular aperture forms two series of fringes at right angles to its sides; their distances being inversely as the widths of the aperture in all directions. There is also a great number of small spectra, regularly distributed in the angular spaces formed by the two series of fringes.

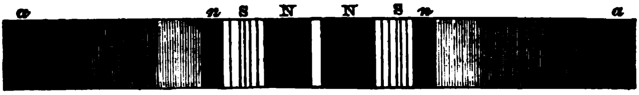
Two small circular apertures placed at a certain distance from one another, form two series of rings just as if each of them existed alone; but if they are close enough to make the rings overlap, the rays proceeding from the two likewise produce, by their interference, a series of very close rectilineal fringes at right angles to the line joining the centres of the apertures, together with two sets of oblique fringes passing through the middle point between these centres. This is the original experiment of Grimaldi already referred to (p. 604).

6. *Diffraction through Gratings or Networks.*—When light, instead of passing through one or two small apertures, passes through a great number of them very close together and regularly distributed, some very remarkable diffraction phenomena are produced, which were discovered by Fraunhofer. Such a system of apertures is called in optical language a **grating** (*réseau*, Fr.; *Gitter*, Germ.).

Fraunhofer formed his gratings:—1. By winding a very fine wire round two parallel screws of equal diameter and very fine thread.—2. By tracing very fine parallel lines on a film of gold-leaf fixed on a plate of glass.—3. By tracing lines with a diamond on a plate of glass, the lines thus formed being opaque, while the intermediate spaces are transparent. This is the method now generally adopted, a dividing engine being used to ensure regularity in the lines. Sometimes the lines are traced on glass covered with a thin coat of varnish, and etched with hydrofluoric acid. When great regularity is desired, the number of lines in a millimetre must not exceed 300, and 38 in that space are sufficient for the complete manifestation of the phenomena.

Effects of Parallel gratings.—A line of light viewed through a grating formed by parallel lines, appears just as it would to the naked eye, excepting that it is somewhat fainter; while on either side is seen a dark space N (*fig.* 652), followed by a spectrum, S, S, having the violet within, and its colours so pure that the principal fixed lines can be easily distinguished in it. Then comes another dark space narrower than the former, then several other spectra more and more extended, but overlapping each other more and more, so that their colours become paler and finally disappear. These spectra may however be separated by viewing them through a prism, the fixed lines then appearing. In homogeneous light, nothing is seen but isolated bands of the colour of the light employed, being in fact the corresponding portions of the several spectra.

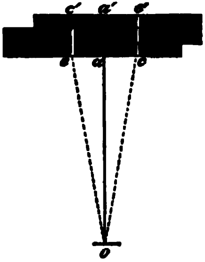
Fig. 652.



Masson has observed that the electric light viewed through a grating exhibits bright lines, as when seen through a prism.

To measure the breadth of these spectra, the grating *o* is placed in front of two parallel slits *e*, *e'* (*fig.* 653), the distance between which admits of variation. Two systems of spectra *ec*, *c'e'* are then seen, which are partly superposed, but may be distinguished by placing one of the slits a little higher than the other. To find the position, or angle of deviation, of any given fixed line, the slits must be separated, or the grating moved farther back, till this line *a*, belonging to the right-hand spectrum formed by the slit *e*, coincides with the same line *a'* in the left-hand spectrum of the same order formed by the slit *e'*. The angle *eoc*, is then equal to twice the angle of deviation sought, viz. $aoe = D$; and the right-angled triangle *aeo* gives $\tan D = \frac{ae}{ao}$, or $D = \frac{ec}{2ao}$, taking the angle for its tangent The angle of deviation is therefore given by the distance between the slits and their distance from the grating.

Fig. 653.



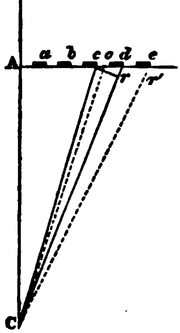
By observations thus made it is found that:—1. The middle points of the successive spectra are equidistant, or in other words, the deviations of these middle points are to one another as the numbers 1, 2, 3, 4, &c.

2. The lengths of the successive spectra, or the distances between two of their corresponding fixed lines, are to one another as the same numbers.

3. The difference of thickness of the opaque and transparent lines has no influence on the position of the spectra, but merely modifies their brightness.

4. The lengths of the spectra depend upon the sum of the widths of an opaque and transparent space taken together; this sum is called an **element** of the grating. The deviation of any given line is inversely as the distance between two elements, or it is proportional to the number of elements in a millimetre. When this number is 100, the first spectrum has the same width as that produced by a flint-glass prism of 60°. Moreover the spaces occupied by the several colours of the spectra are sensibly equal, so that the spectrum thus formed may be called a *normal spectrum*, and may serve as a standard of comparison for the irregular spectra produced by prisms.

Fig. 654.



The preceding laws may be comprised in the general formula, $D = mkN$, where D is the deviation of a fixed line in the spectrum of the *m*'th order, N the number of the elements of the grating in a millimetre, and *k* a constant depending upon the colour in which the line is situated.

To explain the mode of formation of these diffraction spectra, let A*s* (*fig.* 653) be the surface of the grating, *a*, *b*, *c*, *d*, *e* the opaque spaces. Suppose the eye placed at C, and the distance CS of the line of light to be so great, that all the rays proceeding from it to the grating may be regarded as parallel, and the surface of the wave passing by the point A, as coinciding with A*s*. If the grating were removed, the slit *s* would be seen in the direction CS, and no light at all would be seen in any other direction, the elements of interference on the wave A*s*, neutralising one another by pairs. The presence of the grating does not impede the view of the slit, or alter its apparent position, and on each side of the slit there is a dark space, just as if the grating were not there. But at a certain distance A*d*, such that an opaque line of the grating exactly covers the element of the wave which would counteract the action of the preceding element, light will be seen in the direction Cd, the distance Ad being greater in proportion as the eye is farther from the grating. If, for example, the angle ACd is of such a magnitude that $d\mathrm{C} - o\mathrm{C} = o\mathrm{C} - c\mathrm{C} = \frac{1}{2}\lambda$ of the violet, the vibrations communicated to the point C by the element co, will not be destroyed by od, and violet light will be seen in the direction Co, brighter in proportion as the edge of the dark space is nearer to o.

To calculate the deviation $d\mathrm{CA} = d$, describe the arc or having its centre at C; the triangle dcr gives $dr = \lambda = \overline{cd}\ \sin d$; and supposing cd to be contained N times in a millimetre, we have then $1 = \mathrm{N}.\overline{cd}$, and the preceding equation gives $\sin d = \mathrm{N}\lambda$, or taking the angle for the sine, $d = \mathrm{N}\lambda$, which is in fact the general formula of the diffraction-spectra ($\mathrm{D} = mk\mathrm{N}$) applied to the case of the first spectrum. It shows that the deviation is independent of the difference between the opaque and the transparent spaces, and that the constant k is the length of an undulation corresponding to the colour under consideration. For the other colours, we find in like manner $d' = \mathrm{N}\lambda'$, $d'' = \mathrm{N}\lambda''$, &c., λ being greater λ, and λ'' greater than λ' &c. The colours will therefore appear one after the other, at angular distances sensibly proportional to λ, λ', λ'', &c.

Consider, in the next place, another element of the grating at such a distance from A that the difference $d\mathrm{C} - c\mathrm{C} = 2\lambda$, or in general to $m\lambda$, m being a whole number. The interval may then be divided into $2m$ elements of interference corresponding to differences of distance from C, equal to $\frac{1}{2}\lambda$, and these elements being of even number, the actions resulting from their several points would counteract one another two by two, if there were no opaque spaces. But if the opaque spaces cover an *uneven number of elements*, so that an uneven number also remains free, one of these latter will act unopposed, and there will be light in the corresponding direction. The triangle cdr, then gives $d = m\lambda\mathrm{N}$, which is the general formula above given.

It remains to be seen why the light of any particular colour is wanting between the luminous band which corresponds to the difference of distance $m\lambda$ from C, and that which corresponds to $(m + 1)\lambda$. Now between the lines of the grating corresponding to these two bands, two zones may be found in which the differences of distance from the point C increases from $m\lambda$ to $m\lambda + \frac{1}{2}\lambda$, then from this latter to $m\lambda + 2\,.\,\frac{1}{2}\lambda = (m + 1)\lambda$. The rays emanating from the corresponding points of these two zones differ in length of path by $\frac{1}{2}\lambda$, and destroy one another on reaching the point C. Dark bands will therefore occur in the direction of these zones. In white light, however, the colours, by overlapping one another, obliterate all these dark bands, excepting the first two on either side.

If the source of light is too near the grating to allow the rays to be regarded as parallel, the same mode of explanation is still applicable, only it becomes necessary to take account of the difference of path of the contiguous oblique rays at the moment when they reach the grating.

The formula $\sin d = m\mathrm{N}\lambda$, shows that when N$\lambda$ is greater than 1, that is to say when $\frac{1}{\mathrm{N}}$, or an *element* of the grating, is less than λ, $\sin d$ becomes greater than 1, which is impossible; in this case therefore no spectra can be formed, and in fact gratings which have their bars too close do not form any.

If the spectra are observed in any other medium, as when the slit and grating are placed at the opposite ends of a tube filled with water or other liquid, then, if l is the length of an undulation of violet light in that liquid, the deviation will be $d_1 = \mathrm{N}\lambda$, which combined with the equation $d = \mathrm{N}\lambda$, for the deviation of the same part of the spectrum in air, gives $d_1 : d = l : \lambda$, which is the ratio of the indices of refraction in the medium and in air.

Measurement of λ. The equation, $\sin d = \mathrm{N}\lambda$, gives the means of measuring with great accuracy the wave-lengths corresponding to the several fixed lines of the spectrum, which cannot be done with the interference-fringes in Fresnel's experiment (p. 599), because the lines are not distinct. It is by this method that Babinet determined the values given in the table on p. 600.

Irregular Gratings.—Gratings whose bars are totally destitute of regular arrangement produce nothing but a whitish train of light at right angles to the bars: but if the irregularities are subject to a certain law and recur periodically, spectra are produced, whose deviation is expressed by the formula $\sin d = \frac{m\lambda}{\mathrm{L}}$, in which L denotes the space comprising one complete set of bars. The successive spectra then differ greatly in brightness; some are very pale, and, occurring by the side of very bright ones, partly overlap them, but do not perceptibly alter their colours: hence lines may be distinguished in some of these spectra of the higher orders, which cannot be seen in the spectra of the corresponding orders formed by regular gratings, because they are obliterated by superposition. By looking at a candle with the eyes nearly closed, so that the eye-lashes form a grating, a horizontal line of whitish light is generally seen, because the eye-lashes are for the most part at unequal distances; frequently, however, very distinct spectra are produced. Very fine spectra may be seen by looking at the sun or a bright flame through the plume of a crow's feather.

Gratings or Network with square or round bars or meshes.—Gratings with square apertures may be formed of two sets of parallel bars crossing one another. A piece of muslin or riband exhibits such a structure. Such gratings form a great number of small spectra, some disposed along the arms of a cross parallel to those of the squares, others distributed obliquely in the four right angles. The appearance is very brilliant, and varies with the size of the meshes and the distance of the luminous point.

Reflecting Gratings or Striated Surfaces.—When light is reflected from surfaces covered with striæ alternately bright and dull, the same spectra are produced as when it is transmitted through a grating: for the reflected rays are in the same state as if they had been transmitted through the striated surface from a point as far behind as the actual luminous point is before it; the spectra are not, however, quite so bright as those produced by transmission. The iridescence of mother-of-pearl is produced by very fine striæ resulting from its foliated structure; a cast taken of it in soft wax, mastic, or fusible metal, exhibits a similar iridescence. Fibrous gypsum exhibits colours due to the same cause. The feathers of certain birds likewise owe their brilliant colours to diffraction of the light reflected from the very fine filaments of which they are composed.

Half-polished metals sometimes exhibit iridescent colours, due to the parallel striæ produced by the hard powder used in polishing them; but as these striæ are seldom regular, the usual effect is merely a whitish line of light, at the points from which the rays are reflected to the eye. *Barton's buttons*, which are metallic buttons having very fine lines engraved on their surfaces by a peculiar machine, exhibit magnificent diffraction spectra.

Reflection and Refraction.

When a wave of light reaches the surface of separation of two media of different densities, its vibrations are not only propagated onwards into the second medium, but likewise reflected back into the first, each particle of the ether at the surface of separation then becoming a centre of disturbance from which fresh waves spread out in all directions. To find the directions of the reflected and transmitted waves, let MN (*fig.* 655) be the separating surface of two media (air and water, for example), and *SabS′* an incident beam of light of infinitely small section, so that the rays composing it may be regarded as parallel, and the wave-surface, *bc*, perpendicular to their direction, as plane. Now the several points of this wave-surface, *cb*, do not all meet the surface MN at the same instant, but each point, as it reaches that surface, becomes a centre of disturbance from which elementary waves are excited in both the media bounded by MN. Moreover, the velocity of propagation of the waves in the two media is different; because the density of the ether in the one is greater than in the other (pp. 595, 601). Suppose the lower medium to be the one in which the ether has the greater density, and that the velocity of transmission of the light-waves in it is ¾ as great as in the upper. Then, by the time the point *c* of the incident-wave has travelled on to *a*, a wave will have spread out from *b*, in each medium, of a radius *bd* = *ac* in the first, and *bf* = ¾ *ac* in the second; also from any intermediate point *e* (*ea* being a portion of wave-surface parallel to *bc*), a wave will spread out of radius *ed′* = *aa* in the first, and *ef′* = ¾ *aa* in the second. Now each of these elementary waves produces no perceptible effect by itself, a sensible disturbance of the ether or production of light taking place only where a number of them act together, that is to say, in the first medium, along the plane surface *ad*, and in the second along *af*; and straight lines *ar*, *br′*, *aq*, *bq′*, &c., drawn at right angles to these surfaces from the several points between *a* and *b*, will give the direction of the reflected and transmitted rays.

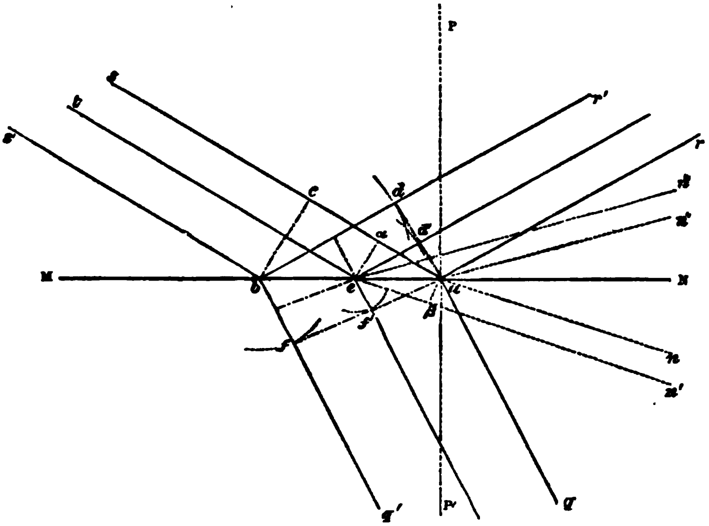
In the first medium, the triangles *abc*, *abd* being equal in every respect, the angle *abd* = the angle *bac*, that is to say, *the incident and reflected rays make equal angles with the reflecting surface, and therefore also with the normal* P*a*. The angles which these rays make with the normal are called the angles of incidence and reflection respectively.

The symmetry of the figure with respect to the plane of incidence, *i.e.* the plane passing through the incident ray and the normal, shows also that *the reflected ray is contained in the plane of incidence.*

The ray which passes on into the second medium is also contained in the plane of incidence, but is bent or refracted out of its previous direction, and does not make the same angle with the normal as the incident ray does. The angle of incidence P*as* = *i* is equal to the angle *cba*, and the angle of refraction P′*aq* = *r* is equal to *baf*;

and the right-angled triangles *abc*, *abf* give $ac = ab \sin i$; and $bf = ab \sin r$; therefore,

Fig. 655.



$\sin i : \sin r = ac : bf$. But the spaces *ac*, *bf* traversed by the ray in the same time, are to one another as the velocities v, v' of light in the two media: hence

$$\frac{\sin i}{\sin r} = \frac{v}{v'}.$$

That is to say, the *sines of the angles of incidence and refraction are to one another in a constant ratio, namely, that of the velocities of light in the two media.* This ratio, which is also that of the lengths of the waves $\lambda : \lambda'$ in the two media, is called the index of refraction, absolute or relative, according as the ray passes from a vacuum into a ponderable medium, or from one ponderable medium to another. The absolute index of refraction of a medium, usually denoted by the letter μ, is the reciprocal of the velocity of light in that medium referred to the velocity in a vacuum as unity; *it is always greater than* 1. If μ, μ' are the absolute indices of two contiguous media, say water and glass, the deflection of a ray passing from the one to the other will be determined by the equation

$$\frac{\sin i}{\sin r} = \frac{\mu}{\mu'},$$

which likewise holds good if μ, μ' are the indices of refraction of the ray in passing from any one medium, as air, into two others, as water and glass.

When μ is greater than μ', that is to say, when the velocity of transmission, or the length of the wave is less in the second medium than in the first, the ray is refracted towards the normal; when μ is less than μ', it is refracted from the normal.

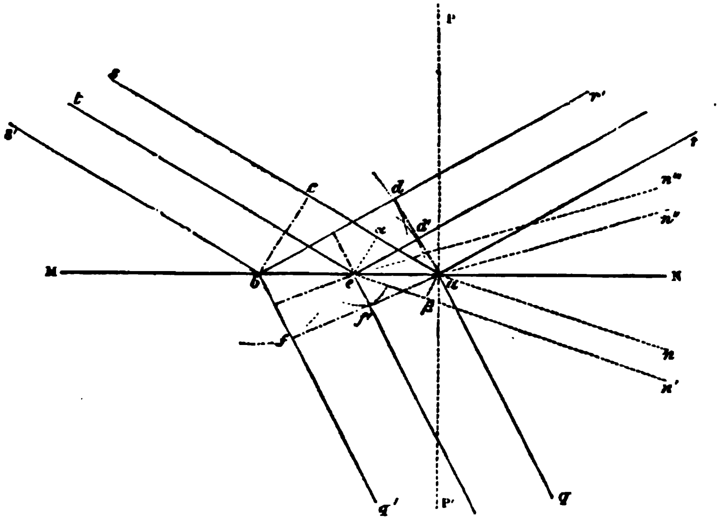
In the latter case, the angle of incidence may be such that the sine of the angle of refraction would be equal to or greater than 1; under such circumstances, the ray does not pass into the second medium at all, but undergoes total reflection into the first. The value of the limiting angle, θ, at which refraction ceases to take place, is given by the equation, $\sin \theta = \frac{\mu}{\mu'} \sin 90° = \frac{\mu}{\mu'}$.

Limitation of the reflected and refracted rays.—The preceding explanations show that there must be reflection and refraction in the directions above determined, but they do not show why the reflected and refracted rays are confined to these directions; for as each point of the surface *ab* (*fig.* 655) is a centre of disturbance, from which waves spread out in hemispheres, it would seem as if rays should be reflected and transmitted in all directions. And such is in fact the case; only, as Fresnel has shown, *all the rays oblique to the reflected and refracted beams rabr', qabq', destroy one another by their mutual interference.*

Suppose *an*, *en'* (*fig.* 654) to be two parallel refracted rays, very close together, but not in the direction determined by the law of the sines. Draw *ea* and *aβ* perpendicular to *sa* and *en'*; then a vibration of the ray *sa*, in reaching the surface *ab*, will have travelled over a space greater by *aa* than the corresponding vibration of the ray *te*; but when the two arrive at the surface *aβ* of the refracted wave, *te* will have moved over a space which, expressed in wave-lengths, is greater, by $\mu . e\beta - aa$, than that passed over by *sa*. Let i be the angle of incidence, *aca*, and ρ the angle of refraction, *eaβ*, of the ray *an*. Then the right-angled triangles *eβa*, *eaa* give $e\beta = ae . \sin \rho$; $aa = ae . \sin i$; therefore $\mu . e\beta - aa = ae\,(\mu . \sin \rho - \sin i)$; and $ae = \dfrac{\mu . e\beta - aa}{\mu . \sin \rho - \sin i}$. Now the rays *an*, *en'* will destroy one another by interference when the difference $\mu . e\beta - aa = \frac{1}{2}\lambda$; therefore, when $ae = \dfrac{\frac{1}{2}\lambda}{\mu \sin \rho - \sin i}$. This shows that *ae* is smaller, or the interfering rays are closer together, the more the ratio $\dfrac{\sin i}{\sin \rho}$ differs from μ; but when it is equal to μ, that is, when the refracted ray is in the direction indicated by the law of the sines, *ae* becomes infinite, and therefore there is no interference.

A precisely similar construction and demonstration, applied to the reflected rays *an''*, *en'''* (*fig.* 655), shows that the contiguous reflected rays destroy each other in all cases excepting when $\sin \rho = \sin i$, that is to say, when the reflected and incident rays make equal angles with the normal. If, however, the point *a* is very close to the left-hand edge of the mirror, the reflected ray *en'* will not exist, and *an* will not be destroyed. Hence if the mirror is very narrow, the rays reflected obliquely to the beam *rabr'* are not completely destroyed, and the reflected beam becomes divergent. Fresnel verified this theoretical deduction by blackening the surface of a mirror, with the exception of a very narrow triangular space. The beam of light reflected from this space was broadest at the narrowest part of the reflecting surface, so that the image which it formed on a screen was a triangle with truncated summit, in a position the reverse of that of the reflecting triangle.

Fig. 655.



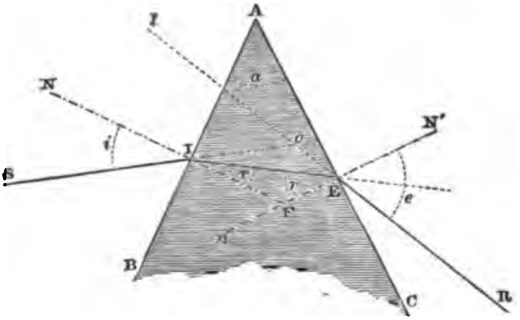
The reflected and refracted beams are always less bright than the incident beam. In fact, they would be together equal in intensity to the incident beam, were it not that part of the light is scattered in all directions, by reflection from minute irregularities on the surface of the medium; and secondly, that a portion of it, often very considerable, is apparently lost by absorption. This process doubtless consists in a communication of the vibratory motion of the ether to the particles of the ponderable body itself, the particles thus set in motion again acting as centres of vibration, and exciting fresh undulations in the surrounding ether, thereby rendering the body visible. The vibrations excited in the particles of a ponderable body by the movements of the ether likewise produce numerous changes in the state of the body itself, raising its temperature, and setting up certain chemical actions within it, which will be afterwards more fully considered. It is true that the ether transmits vibratory movements which render bodies hot, and others which determine chemical changes in them without directly rendering them visible; but it is probable that the luminiferous waves themselves likewise alter the thermic and chemical conditions of a body, that is to say, excite in the molecules of the body, vibrations which result in thermic and chemical changes, and do not again excite luminiferous waves in the ether. In other words, a certain amount of light is lost in producing heat and chemical change. In passing through a transparent medium, such as glass or water, with polished surface, and very little colour, the amount of light lost by absorption is but small; coloured media transmit certain rays and reflect or absorb others. When light falls on the surface of an opaque body, such as a metal, the path of the refracted ray cannot be followed, inasmuch as it is completely absorbed by an extremely thin stratum of the surface.

The general laws of reflection and refraction having been established, the application of them to determine the path of a reflected or refracted ray under any given circumstances is a problem of pure geometry, into which we do not propose to enter in this article, further than to speak of refraction through prisms, which is of special importance in the determination of indices of refraction.

A **prism**, in optical language, is a transparent medium, bounded by plane surfaces, not parallel to one another. The edge in which these surfaces meet, or would meet, if produced, is called the **refracting angle** of the prism. Solid prisms for optical use are generally made either of glass or of rock-crystal, and with triangular section. Such a prism has three refracting angles, which may be either equal or unequal. The face of a triangular prism opposite the refracting angle is called the **base**. Liquid prisms are made by inclosing a transparent liquid in a wedge-shaped glass, having its inclined sides formed of plate glass. One of the sides may be made to move on a hinge so as to vary the refracting angle.

Let us now trace the course of a ray of light through a prism. If BAC (*fig.* 656) be a prism of glass or any transparent material of greater refracting power than the surrounding medium, a ray SI, entering at I, and making an angle i with the normal, NIF, will be refracted within the prism in the direction IE, making with the normal an angle r less than i. This ray emerging at E, will pass on in the direction ER, making with the normal to the face AC, an angle e greater than the angle r' which IE makes with the same normal. The final result is to bend the ray away from the refracting angle, or towards the base of the prism; accordingly an eye placed at R will see an object S in the direction REl, as if it had been moved upwards towards the summit of the prism. The angle Sol = D contained between the incident and emergent rays is called the **angle of deviation**. It is evidently equal to the sum of the angles IEo, EIo; that is, $D = i - r + e - r'$. But the triangle IEF shows that $r + r' =$ IFn, the angle contained between the two normals, and therefore to the refracting angle of the prism, a. The deviation is therefore given by the formula:

Fig. 656.



$$D = i + e - a.$$

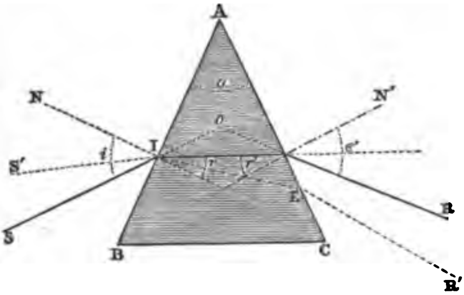
For a given angle of incidence i, it increases with the refracting angle of the prism for suppose a to be increased by δ, then since r is constant, and $r + r' = a$, r' must also increase by δ, and therefore e by $\mu\delta$, μ being greater than 1; that is to say, e increases more than a, and consequently D increases.

When the refracting angle is constant, the deviation varies with the angle of incidence, and attains a *minimum* value when the incident and emergent rays make equal angles with the refracting surfaces. To show, in the first place, that this latter condition is possible, suppose that an incident ray coinciding with the normal NI (*fig.* 657) is gradually inclined into the position SI; the angle r, which is at first equal to 0°, will also increase continually, and therefore r' must diminish, since $r + r' = a$; moreover since a must be less than 180°, and r may increase to 90°, the incident ray must eventually come into a position in which $r = r'$, and therefore $i = e$.

Now let SI and ER (*fig.* 657) be the rays which make equal angles with the normals; and suppose that SI moves into the position S'I closer to the normal; r will then diminish.

and therefore r' must increase by the same quantity; e will therefore also increase, and become greater than i. But $\frac{\sin i}{\sin r} = \frac{\sin e}{\sin r'}$; and since $\sin e$ and $\sin r'$ are greater than $\sin i$ and $\sin r$, the difference between $\sin e$ and $\sin r'$ must be greater than that between $\sin i$ and $\sin r$; *a fortiori*, therefore, the angles e and r' must differ more than i and r. The angle e has therefore increased more than i has diminished, and consequently the deviation, $D = i + e - a$, must also have increased. In a similar way, it may be shown that if the incident ray enters below SI, the increase of i will be greater than the diminution of e. The deviation is therefore increased by shifting the ray SI either way from its position, that is to say, *the deviation is a minimum when the incident and emergent rays are equally inclined to the surfaces of the prism, or to the normals.*

Fig. 657.



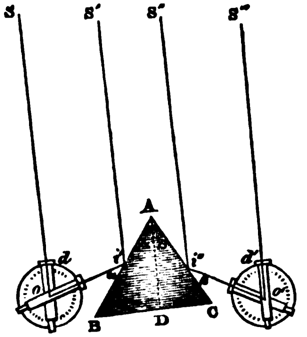
In this case, the expression for the deviation becomes $D = 2i - a$, which gives $i = \frac{a + D}{2}$; also, since r and r' are equal, we have $r = \frac{a}{2}$: hence also:

$$\mu = \frac{\sin i}{\sin r} = \frac{\sin \frac{1}{2}(a + D)}{\sin \frac{1}{2} a};$$

an expression which gives the index of refraction of the medium forming the prism, as a function of the refracting angle of the prism and the angle of minimum deviation. This affords one of the best means of determining indices of refraction.

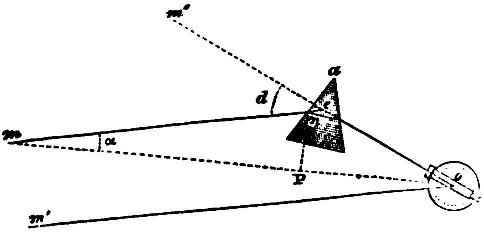
Measurement of the Index of Refraction of Solids and Liquids.— 1. To measure the angle of the prism: the prism ABC (*fig.* 658) is fixed in such a manner that its edges may be perpendicular to the divided circle of a theodolite o; and a mark S, placed at such a distance that the rays proceeding from it may be regarded as parallel, is viewed through the telescope, first by reflection from AB, then directly, and the angle $S o i = d$ is measured. The theodolite is then moved to o', and the same mark is viewed directly and by reflection from AC, and the angle $S''' o i = d'$ is measured. Half the sum of these two angles is the measure of the angle A. To show this, draw AD parallel to the direction of the incident rays, and dividing the angle A into two parts, α and β. Then $\alpha = S'iA = oiB$, and therefore $2\alpha = 180° - S'io$. But $Soi = d = 180° - S'io$; therefore $d = 2\alpha$. In like manner it may be shown that $d' = 2\beta$; consequently $\alpha + \beta = A = \frac{1}{2}(d + d')$.

Fig. 658.



2. To measure the minimum deviation, the prism is fixed on a support capable of turning on a vertical axis. A very distant mark m (*fig.* 659) is viewed with the theodolite o, first directly in the direction om, then through the prism in the direction om''; and the prism is turned round till the angle mom'' between these two directions is reduced to its smallest possible magnitude. The angle so determined is the angle of minimum deviation, provided the mark is so distant that the rays proceeding from it may be regarded as parallel. A distant lightning-conductor forms a very good mark for the purpose in the day-light; a slit in the shutter of a dark room, provided the room be large, may also be used.

Fig. 659.



Observations are made by artificial light, with a lamp surrounded by a jacket of tin plate having a vertical slit.

In this last case, the mark is seldom far enough off to allow the divergence of the rays to be neglected. Let α be the angle of divergence, and o the angle mom''. The triangle mco gives,

$$180^\circ = a + o + (180^\circ - m''cm) = \alpha + o + 180^\circ - (2i - \alpha).$$

This gives $i = \frac{1}{2}(a + o + \alpha)$, and therefore

$$\mu = \frac{\sin \frac{1}{2}(a + o + \alpha)}{\sin \frac{1}{2}a.}$$

The angle α may be measured by transporting the theodolite to m. But as α is very small, it is generally considered sufficient to measure the length of the perpendicular nP and the distance mP, by stretching a cord from o to m; then $\tan \alpha = \frac{nP}{mP}$.

A very convenient method of obtaining parallel rays is by the use of the collimator, an instrument consisting of a telescope-tube blackened inside, and having two wires, one vertical, the other horizontal, fixed within it, and crossing in its axis. When the tube is directed towards a window, the wires, being illuminated by a beam of parallel rays, form a shadow which may be regarded as an object placed at an infinite distance. If a convex lens be placed at one end of the tube, and the cross-wires in its principal focus, the collimator may be used in the same manner for observations with artificial light: for when the other end of the tube is directed towards a lamp, the rays crossing each other at the intersection of the wires will issue parallel after passing through the lens, and will therefore be brought to a focus by another telescope just like those proceeding from a celestial object.

In all observations of indices of refraction, it is necessary to specify the colour of the light to which the observation refers. Solar light, and lamp, candle, or gas light are in fact of composite nature, and separable by refraction into coloured rays of unequal refrangibility; consequently, any line of light viewed through a prism appears widened and fringed with bands of colour parallel to its edges. It is usual to make the observations on the yellow rays, which are situated towards the middle of the coloured image, or spectrum, and possess the greatest brightness. But as each colour occupies a certain breadth in the spectrum, and the boundaries of the several colours are not very well defined, it is by no means certain that two observations made on the same colour will refer to exactly the same part of the spectrum. The difficulty thence arising is however completely removed by the observation of certain fine dark lines, discovered by Fraunhofer, in the solar spectrum (p. 620), which are parallel to the lines of separation of the different colours, and are always disposed in the same manner in each colour, whatever may be the nature of the prism. The spectra of flames and of the electric light exhibit bright bands, likewise of fixed position for each particular source of light.

A very sharply defined mark may be obtained without recourse to the fixed lines, by replacing the vertical wire of the collimator with a sewing needle. The coloured bands parallel to the edges of the needle overlap one another towards the point, forming a well-defined line of separation between two very distinct colours, a bluish-green and a deep rose tint. (H. Deville.)

Determination of Refractive Indices by Interference.—The displacement of the fringes in Fresnel's experiment (p. 600) furnishes a very delicate method of determining indices of refraction. A thin film of the transparent substance being placed before one of the mirrors (*fig.* 645), so as to intercept part of the pencil of rays reflected from it, the number of ranks through which the central fringe is displaced is observed. Let R be this number, e the thickness of the film, m and m' the number of wave-lengths, λ and λ', included within the thickness e of the air and the transparent film: then

$$e = m\lambda = m'\lambda'; \text{ whence } \frac{m'}{m} = \frac{\lambda'}{\lambda} = \frac{v'}{v} = \mu.$$

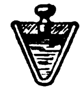
But, since the central band is displaced through R ranks, we have also $m' = m + R$, each additional wave-length in the film displacing the central band one rank further. Consequently,

$$\mu = \frac{m}{m} = \frac{m + R}{m} = \frac{e + R\lambda}{e},$$

a formula which gives the index of refraction in terms of the thickness of the film and the wave-length.

This method is especially applicable to gases and vapours (p. 618).

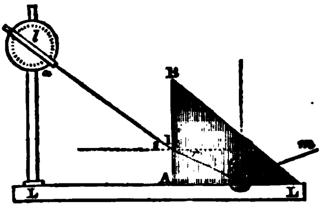
Fig. 660.



Determination of the Index of Refraction of Liquids.—1. By the method of *least deviation.* The liquid is inclosed in a wedge-shaped vessel, of which *fig.* 660 represents a transverse section. The sides are formed of thin plate-glass, and it is essential to the accuracy of the observations that the two faces of each of these plates should be parallel. As, however, this condition is seldom completely fulfilled, it is necessary to measure the deviation produced by the prism when empty, previous to making the observation with the liquid to be examined. The first deviation is then to be deducted from, or added to the second, according as it is in the same or in the contrary direction.

As liquids are very expansible by heat, their indices of refraction may be sensibly affected, even by variations of temperature not exceeding those of the surrounding atmosphere. It is necessary, therefore, to make the observations at a constant temperature, to agitate the liquid briskly before making the observation, and to avoid using the direct rays of the sun, which might heat it unequally in passing through it.

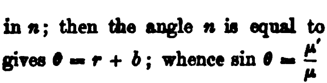
Fig. 661.



2. *By total reflection.*—This method is especially applicable to very small quantities of liquid; also to imperfectly transparent liquids and pasty substances, such as the crystalline lens of the eye. A small drop of the liquid is attached to the lower surface of a right-angled prism BAL (*fig.* 660), resting on a horizontal rule LL, in which a hole *o* is made to receive the drop. The prism must be formed of a substance of known refractive index, greater than that of the liquid. The drop of liquid is viewed through the prism by means of a small telescope *l*, turning on the centre of a graduated circle which slides up and down a vertical rule L*l*, fixed to the table. The telescope is at first fixed at such a height, that objects below the drop are seen through it; but on gradually lowering the divided circle, the angle I*on* continually increases, and at last the rays coming from the other side of the prism at *m* are totally reflected at *o*. The telescope is then fixed, and the angle α is observed. The angle *no*I is then equal to the the limiting angle θ, and $\sin\theta = \frac{\mu'}{\mu}$, μ being the refractive index of the prism, and μ' that of the liquid. Now the angle $\theta = 90° - r$; therefore $\sin i = \cos\alpha = \mu \sin r = \mu \cos\theta$; hence $\cos\theta = \frac{\cos\alpha}{\mu}$, and $\sin\theta = \frac{1}{\mu}\sqrt{\mu^2 - \cos^2\alpha} = \frac{\mu'}{\mu}$; therefore

$$\mu' = \sqrt{\mu^2 - \cos^2\alpha}.$$

Fig. 662.



Wollaston devised a modification of this method by which the refractive index may be determined without calculation (see Miller's *Elements of Chemistry*, 3rd ed. i. 155; and Daguin, *Traité de Physique*, 2^{me} ed. iv. 160). The slight trouble of calculation from the preceding formula is not, however, a serious objection to the method. A more important objection arises from the difficulty of making the prism exactly rectangular. To obviate this difficulty, Malus uses an acute-angled prism (*fig.* 662), the angle *b* of which is known. The observation being made as above described, we have, as before, $\beta = 90° - \alpha$ and $\sin\theta = \frac{\mu'}{\mu}$. Let the normal *In* be produced to meet the normal *nn'* in *n*; then the angle *n* is equal to the angle *b* of the prism, and the triangle I*no* gives $\theta = r + b$; whence $\sin\theta = \frac{\mu'}{\mu} = \sin(r + b) = \sin r \cos b + \sin b \cos r$. But $\mu \sin r = \sin i$; and the triangle I*n'n* gives $n\text{I}n = i + \beta = 90° - b$; whence $i = 90° - (b + \beta)$: therefore

$$\sin r = \frac{1}{\mu}\cos(b + \beta);$$

and

$$\cos r = \frac{1}{\mu}\sqrt{\mu^2 - \cos^2(b + \beta)}.$$

This gives;

$$\mu' = \mu \sin\theta = \cos(b + \beta)\cos b + \sin b\sqrt{\mu^2 - \cos^2(b + \beta)}.$$

This method may also be applied to solids. Soft bodies like wax, or gelatinous organic bodies may be at once attached to the lower surface of the prism. Hard bodies may be attached by means of a liquid of *greater refracting power* than the prism: the total reflection will then take place just as if the solid were immediately attached.

The same method also gives the index of refraction of the prism itself, the observation being made without applying any liquid to the lower face. In this case, since the medium below the prism is air, we have $\mu' = 1$, and the formula gives

$$\mu = \frac{1}{\sin b}\sqrt{1 + \cos^2(b+\beta) - 2\cos b\cos(b+\beta)}.$$

The following tables contain the indices of refraction of several solids and liquids, determined by the preceding methods. They all relate to the yellow rays of the spectrum, excepting those of Wollaston, which relate to the extreme red:

Indices of Refraction of Solids.

Name of substance.	Index of refraction.	Observer.
Chromate of lead	2·50 to 2·97	Brewster.
Diamond	2·47 to 2 75	Br.; Rochon.
Phosphorus	2·224	Brewster.
Glass of antimony	2·216	„
Sulphur (native)	2·115	„
Zircon	1·95	Wollaston.
Borate of lead	1·866	Herschel.
Carbonate of lead	1·81 to 2·06	Brewster.
Ruby	1·779	„
Felspar	1·764	„
Tourmalin	1·668	„
Topaz, colourless	1·610	Biot.
Beryl	1·598	Brewster.
Tortoise-shell	1·591	„
Emerald	1·585	„
Flint glass	1·57 to 1·58	Br.; W.
Rock-crystal	1·547	Wollaston.
Rock-salt	1·545	Newton.
Apophyllite	1·543	Brewster.
Colophony	1·543	Wollaston.
Sugar	1·535	Wollaston.
Phosphoric acid	1·534	Brewster.
Sulphate of copper	1·531 to 1·552	„
Canada balsam	1·532	Young.
Citric acid	1·527	Brewster.
Crown glass	1·525 to 1·534	„
Nitre	1·514	„
Plate-glass	1·514 to 1·542	„
Spermaceti	1·503	Young.
Crown glass	1·500	Wollaston.
Sulphate of potassium	1·500	Brewster.
Ferrous sulphate	1·494	„
Tallow; wax	1·492	Young.
Sulphate of magnesium	1·488	Brewster.
Iceland spar	1·654	Malus.
Obsidian	1·488	Brewster.
Gum	1·476	Newton.
Borax	1·475	Brewster.
Alum	1·457	Wollaston.
Fluor spar	1·436	Brewster.
Ice	1·310	Wollaston.
Tabasheer	1·1115	Brewster.

Indices of Refraction of Liquids.

Name of liquid.	Index of refraction.	Observer.
Sulphide of carbon	1·678	Brewster.
Oil of cassia	1·031	Young.
Bitter almond oil	1 603	Brewster.
Nut-oil	1·500	„
Linseed-oil	1·485	Wollaston.
Oil of naphtha	1·475	Young.
Rape-oil	1·475	Brewster; Young.
Olive-oil	1·470	Brewster.
Oil of turpentine	1·470	Wollaston.
Oil of almonds	1·469	„
Oil of lavender	1·457	Brewster.
Sulphuric acid (specific gravity 1·7)	1·429	Newton.
Nitric acid (specific gravity 1·48)	1·410	Young; Wollaston.
Solution of potash (specific gravity 1·410)	1·405	Fraunhofer.
Hydrochloric acid (concentrated)	1·410	Biot.
Sea-salt (saturated)	1·575	„
Alcohol (rectified)	1·372	Herschel.
Ether	1·358	Wollaston.
Alum; saturated	1·356	Herschel.
Human blood	1·354	Young.
White of egg	1·351	Euler, jun.
Vinegar, distilled	1·372	Herschel.
Saliva	1·339	Young.
Water	1·336	Wollaston; Brewster.

The indices of refraction assigned to the same substance by different observers often exhibit considerable diversities, arising partly from imperfection of method, but especially from want of chemical or physical identity in the substances examined.

A comparison of the indices of refraction of different substances leads to but few general conclusions. One of the most remarkable is that inflammable substances are strongly refractive: *e. g.*, sulphur and phosphorus among solids; oils and hydrocarbons among liquids; it was the observation of this fact that led Newton to infer that the diamond would be found to contain an inflammable principle.

Generally speaking, the refracting power of *any one substance* increases with its density; though it is by no means true that the refracting powers of different substances are proportional to, or even follow in the same order as their densities. Jamin found, by a method presently to be noticed, that the refracting power of water is increased by compression. On the other hand, the refracting power of liquids is diminished when they are expanded by heat. Brewster found that the index of refraction of common ether, which, at ordinary temperatures, is equal to 1·358, is reduced to 1·057 when the volume of the ether is tripled by heat. Numerous experiments on this subject have been made by Dale and Gladstone (Phil. Trans. 1858; Ann. Ch. Phys. [3] lviii. 117), who operated on twelve different liquids between the temperatures of 3° and 50', using the method of minimum deviation. The prism was placed horizontally and heated by a spirit-lamp or cooled by a freezing mixture. The temperature was indicated by a thermometer with which the liquid was stirred. The following table contains a portion of the results (see also page 625); they relate to the line D of the solar spectrum, excepting those with phosphorus, which relate to the line C:

Temperature.	Sulphide of carbon.	Water.	Ether.	Alcohol, absolute.	Methyl-alcohol.	Phosphorus, liquid.	Oil of Cassia.
0°	1·6442	1·3330					
10	1·6346	1·3327	1·3592	1·3658	1·3379		
20	1·6261	1·3320	1·3545	1·3615			
30	1·6182	1·3309	1·3495	1·3578	. .	2·0741	
40	1·6103	1·3297	. .	1·3536	1·3297	2·0677	1·5796
50	. .	1·3280	. .	1·3491	. .	2·0603	
60	. .	1·3259	. .	1·3437	. .	2·0515	1·5690

The refractive index of *water* diminishes continuously between − 1·3° and + 5·2°, the direction of the variation not changing in the passage through the point of maximum density. (Arago. Jamin. Dale and Gladstone.)

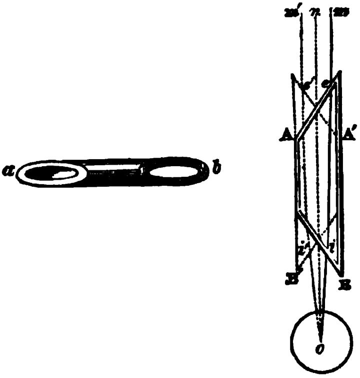
In the passage of a body from the solid to the liquid state, the refractive index sometimes diminishes, as in the case of *phosphoric acid*, *wax*, and *tallow*. Sometimes it increases, as with *water* and *borax;* sometimes again it does not change perceptibly, as is the case with *sugar*.

H. Deville (Ann. Ch. Phys. [3] v. 129) has measured the index of refraction of *alcohol*, *wood-spirit*, and *acetic acid*, mixed with water in different proportions. These substances exhibit the greatest degree of contraction, or of density, when united with $\frac{3}{2}$ at. water (*e. g.*, $2C^2H^6O.3H{\cdot}O$). It is also with this proportion of water that wood-spirit and acetic acid exhibit the highest degree of refractive power, whereas with alcohol this is the case when it contains $\frac{1}{2}$ at. water ($2C^2H^6O.H^2O$). At 16° the refractive index of absolute alcohol is 1·3663; that of $2C^2H^6O.H^2O$ is 1·3662; that of anhydrous methylic alcohol, CH^4O, is 1·3358; of $2CH^4O.3H^2O$, 1·3462; that of anhydrous acetic acid, $C^4H^6O^3$, is 1·3753; and of $2C^4H^6O^3.3H^2O$, 1·3781.

Index of Refraction of Gases. Refractive Power. Biot and Arago determined the refractive index of atmospheric air, by the method of minimum deviation, using a hollow glass prism, called a *Borda's prism*, consisting of a glass tube (*fig.* 663) 4 or 5 centimetres in diameter, and having its ends *a*, *b* cut in a slanting direction and closed with very thin plates of parallel glass. The prism was mounted, with its refracting angle vertical, on a brass tube connected with a stop-cock and screwed on to the plate of an air-pump. The pressure of the air in the tube was measured by connecting it with a siphon-gauge. The tube having been exhausted, filled with dry air several times, and again exhausted, observations were made with it similar to those described at p. 612; with this exception however, that as the refracting power of the exhausted prism was less than that of the surrounding air, the *maximum*, instead of the *minimum* deviation was observed. The deviations being extremely small, the thickness of the prism prevented the mark from being viewed directly. To obviate this difficulty, after the mark had been viewed through the prism represented in section at AB, and the maximum deviation of the ray *meio* observed, the prism was moved half round into the position

A'B, and the same mark again observed. The image *m* was thereby thrown to the opposite side of the ray *no* proceeding directly from the object, so that the angle *ioi'* was equal to twice the angle *noi*. This method gave for the index of refraction of air at 0° C. and 0·76 met. barometric pressure, referred to a vacuum as the unit, the number 1·00294.

Fig. 663.



In like manner, the indices of refraction of other gases were determined, referred to that of air as unity.

Now on measuring in this manner the refraction produced by air or other gases at different densities, it was found that, at pressures not exceeding that of the atmosphere, the quantity μ^2-1, which is called the **refractive power**, is proportional to the density of the gas—in other words, that $\frac{\mu^2-1}{d}$, which may be called the **specific refractive power**, is a constant quantity. The law was not verified for pressures greater than that of the atmosphere, on account of the difficulty of retaining condensed gases within the hollow prism.

Dulong determined the refractive powers of a considerable number of gases and vapours by the following method, founded on the proportionality of the refractive power to the density. A distant mark is observed by a telescope through a Borda's prism filled with dry air, at a pressure h. The prism and telescope are then fixed, and the prism is filled with another gas, the pressure of which is varied till the image of the mark again coincides with the wire of the telescope. The refractive index of the gas under the pressure h', is then equal to that of the air under the pressure h. If then μ' and μ are the indices of refraction of the gas and of air at the same pressure h, and at the same temperature, we have, since the index of the gas under the pressure h' is equal to μ,

$$\mu'^2-1 : \mu^2-1 = h : h',$$

whence μ' is easily found.

Refractive power of Gases.

Name of gas.	Refractive power.			Index of refraction.	Density.
	Compared with that of air.	Excess over calculation.	Absolute. μ^2-1.		
Air	1·000	. .	0·000589	1·000294	1·000
Oxygen	0·924	. .	0·000544	1·000272	1·106
Hydrogen	0·470	. .	0·000277	1·000138	0·069
Nitrogen	1·020	. .	0·000601	1·000300	0·971
Chlorine	2·623	. .	0·001545	1·000772	2·470
Nitrous oxide	1·710	+ 0·228	0·001007	1·000503	1·520
Nitric oxide	1·030	+ 0·058	0·000606	1·000303	1·039
Hydrochloric acid	1·527	+ 0·020	0·000899	1·000449	1·247
Carbonic oxide	1·157	. .	0·000681	1·000340	1·957
Carbonic anhydride	1·526	−0·093	0·000899	1·000449	1·524
Cyanogen	2·832	. .	0·001668	1·000834	1·806
Ethylene	2·302	. .	0·001356	1·000678	0·978
Marsh gas	1·504	. .	0·000886	1·000443	0·555
Chloride of ethyl	3·720	−0·099	0·002191	1·001095	2·234
Hydrocyanic acid	1·531	−0·130	0·000903	1·000451	0·944
Ammonia	1·309	+ 0·093	0·000771	1·000385	0·596
Phosgene	3·936	+ 0·152	0·002318	1·001159	3·442
Sulphydric acid	2·187	. .	0·001288	1·000644	1·191
Sulphurous anhydride	2·260	. .	0·001331	1·000665	2·234
Ether	5·197	. .	0·003061	1·900153	2·580
Sulphide of carbon	5·110	. .	0·003010	1·000150	2·644
Phosphoretted hydrogen	2·682	. .	0·001579	1·000789	1·214

By this method **Dulong** has shown: 1. That the refractive power of a mixture of gases is equal to the mean of those of the constituent gases calculated for the pressure to which each gas is actually subjected in the mixture. 2. That the refractive power of a compound gas is not equal to the mean of those of the component gases, but is sometimes greater and sometimes less. The third column of the following table exhibits the differences *between* the actual refractive powers of certain compound gases, and those which would be obtained by adding together the refractive powers of the several components, and dividing by the volume of the compound gas. The refractive power of atmospheric air is found to be exactly the mean of those of its two constituent gases, a fact which shows, together with others, that the air is a mixture, and not a compound of oxygen and nitrogen.

The numbers in this table show that there is no simple relation between the refractive powers of different gases and their densities; hydrochloric acid gas, for example, has a lower density, but much higher refractive power than sulphurous anhydride, and ether-vapour has about the same density as chlorine, but double the refractive power.

The **interferential method**, the principle of which has been already described, is very well adapted to the measurement of the refractive indices of gases, and gives results more exact than those of the preceding methods. Arago and Fresnel applied it to the comparison of the refractive indices of moist and dry air. The interfering rays were made to pass through two copper tubes, each a metre in length, and closed at the ends with glass plates having exactly parallel faces, the one being filled with moist and the other with dry air. The fringes were then found to be displaced to the amount of one band and a quarter on the side of the dry tube, showing that moist air is rather less refractive than dry air. *Precipitated vapour* was found to produce a very slight increase in the refracting power of the air.

An improved apparatus for experiments of this kind has been constructed by **Jamin**, but we must refer for the description of it to his memoir (Ann. Ch. Phys. [3], xlix. 382), or **Daguin's** *Traité de Physique*, iv. 402. By means of this apparatus, Jamin has shown that vapour of water, at the temperature of 0° and at 0·76 met. barometric pressure, supposing it could exist under those circumstances, would have an absolute index of refraction equal to 1·00261, which is less than that of air at the same temperature and pressure. The refractive power of aqueous vapour calculated by the formula $\mu^2 - 1$ is therefore = 0·000521.

By adding to the refractive index of dry air that of aqueous vapour in the saturated state, under the pressure which it possesses at 20°, Jamin finds that the difference between the refractive indices of dry air and air saturated with aqueous vapour is only 0·000000726, a quantity which is too small to produce any sensible effects with Borda's prism, and may be safely neglected in the calculation of atmospheric refraction for astronomical purposes.

Refractive power of vapours produced at high temperatures. **Leroux** (Ann. Ch. Phys. [3], lxi. 385) has measured the refractive indices of a few of these vapours by the method of least deviation, using a hollow prism of iron having part of its opposite faces replaced by flat glass plates, and provided with proper appliances for heating, and for keeping the pressure of the vapour equal to that of the atmosphere. The indices and refractive powers of the vapours examined are as follows:

Substance.	Absolute index of refraction.	Refractive power $\mu^2 - 1$.
Sulphur . . .	1·001629	0·003258
Phosphorus . .	1·001364	0·002728
Arsenic . . .	1·091114	0·002228
Mercury . . .	1·000556	0·001112

Dispersion.

When a narrow beam of the sun's rays is passed through a glass prism (*fig.* 664) and received upon a screen, an elongated image or **spectrum** is formed, exhibiting a series of brilliant colours in the following order:

Red. Orange. Yellow. Green. Blue. Indigo. Violet.

the red occupying the lowest or the highest place, according as the refracting angle of the prism is turned downwards or upwards. The different coloured rays are therefore refracted by the prism in different degrees, the red exhibiting the least, and the violet the greatest deviation. Moreover, if a small hole be made in any part of the screen so as to allow a narrow beam of the rays of any one colour to pass, and this beam be transmitted through another prism, it will not again be elongated and split up into different colours, but will form upon a second screen an image of the same shape as the aperture, and of the same colour as the beam before passing through the second prism. In this second refraction also, the red exhibits the least, the violet the greatest deviation.

Fig. 664.

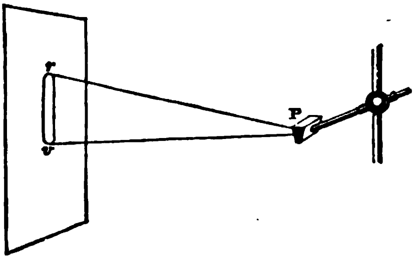
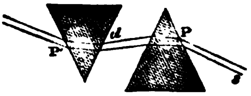


Fig. 665.



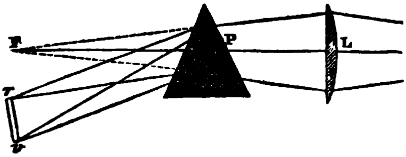
It was by observations of this kind that Newton made the grand discovery, that *Solar light may be separated by refraction into a number of rays of different colours, and that to each colour there corresponds a distinct degree of refrangibility, the red rays being the least, the violet the most refrangible, and the intermediate colours increasing regularly in refrangibility from the red to the violet.*

This result is confirmed by the fact that the reunion of the colours of the spectrum produces white light. This may be shown by receiving the beam of light *s*, refracted by a prism P (*fig.* 665), on a second prism P' of the same substance and having the same refracting angle. The rays are thus brought back to parallelism and form a beam of white light. A very simple apparatus for exhibiting this recomposition of white light is a rectangular glass trough divided in halves by a diagonal glass partition On pouring water into one of the divisions and passing a beam of sunlight through it, a coloured spectrum is formed; but on pouring water into the second division, the rays are brought back to parallelism, and the emergent beam is white.

Another mode of demonstrating the recomposition is to colour a circular piece of card-board in sectors with the tints of the spectrum, and give it a rapid rotatory motion. If the disc revolves in less than the tenth of a second (the time during which an impression remains on the retina) the whole surface appears of a uniform greyish-white tint, the deviation from perfect whiteness arising from the impossibility of exactly imitating the colours of the spectrum by pigments.

To obtain a complete separation of the colours of the spectrum, the prism should have a large refracting angle, and the aperture should be as narrow as possible: for a wide aperture may be regarded as a number of narrow ones side by side, each of which produces its own spectrum, the colours of the several spectra thus formed overlapping each other and producing compound tints; indeed, if the aperture exceeds a certain width, the middle of the image will receive rays of all colours and will appear white. For the same reason, the beam of light must not be divergent, and the apparent diameter of the luminous body from which the light proceeds must be as small as possible: for the incident light passing through a very small aperture is more divergent as the apparent diameter of the source of light is larger; the sun's rays passing through such an aperture form a cone having a vertical angle of 30 minutes. Newton obtained a very bright and pure spectrum by passing a broad and thick rectangular beam of light through a convex lens L (*fig.* 666) of long focus, placed very near the prism P, and receiving the light on a white screen placed in the focus of the lens. Each colour is then brought to a focus on the screen, forming a bright narrow spot, the whole producing a very pure spectrum *rv*. An improvement on this arrangement is to use a cylindrical lens parallel to the edges of the prism, whereby the rays of each colour are collected into a thin focal band well separated from the rest. Foucault has made a further improvement by interposing, between the lens and prism, a diaphragm, to stop the rays which would pass too near the edge of the lens, and diminish the sharpness of the coloured images. The spectrum is more elongated in proportion as the lens is placed nearer to the prism, which is then farther from the screen, the latter being placed at a determinate distance from the lens.

Fig. 666.



To obtain a beam of perfectly homogeneous light, a coloured beam passing through a small hole in the part of the screen on which the spectrum produced as above is received, is transmitted through a second prism; and if the deflected image thus formed is at all elongated, showing that the original coloured beam was not quite homogeneous, the light of a portion of it must be passed through an aperture in a second screen placed to receive it. A ray thus separated will be found to be perfectly homogeneous in colour, and of uniform refrangibility.

Instead of receiving the spectrum on a screen, it may be viewed directly by holding the prism between the eye and the source of light, the red rays then appearing in the highest or lowest position according as the refracting angle of the prism is held downwards or upwards. The spectrum may also be magnified by viewing it through a telescope. These methods enable us to view the spectra of sources of light not bright enough to throw a visible image on a screen, such as the light reflected from a strip of white paper on a dark ground.

The spectra of the moon and planets, and of white terrestial objects illuminated by solar light, are similar to that obtained with the direct rays of the sun. The spectra of the fixed stars exhibit the same colours and nearly in the same proportions. Those of ordinary flames (hydrocarbon flames) likewise exhibit the same colours, but with a larger proportion of yellow. That of an alcohol flame consists mainly of yellow light, and if a little common salt be mixed with the alcohol, the flame gives a perfectly monochromatic yellow light. The flame of a Bunsen's burner in which a salt of lithium is ignited, gives a spectrum consisting almost wholly of red light; and when a salt of thallium is ignited in it, the spectrum consists wholly of green light.

Fixed Lines in the Solar Spectrum.

Newton, by passing a beam of light proceeding from a small circular aperture through a prism, obtained a spectrum which appeared perfectly continuous, whence he concluded that white light contained rays of all degrees of refrangibility, regularly increasing from the red to the violet. But **Wollaston** in 1802, by looking through a good flint glass prism at a very narrow rectangular aperture illuminated by sun-light, perceived that the spectrum was intersected by several very fine dark lines parallel to the edges of the prism, or to the boundary lines of the several colours; and fifteen years afterwards, **Fraunhofer** of Munich, without being acquainted with Wollaston's observations, made the same discovery by viewing a spectrum formed in the manner just described through a telescope. The lines were very fine, all dark, and some perfectly black, and Fraunhofer was able to count between 500 and 600 of them, their number increasing with the magnifying power of the telescope. These lines are distributed irregularly throughout the whole length of the spectrum, and do not, for the most part, occur at the limits of the principal colours. Eight of them, easily distinguished by their position and intensity, are denoted by the first eight letters of the alphabet, beginning from the red of the spectrum: they are shown in *fig.* 667. Some of them, when examined by a good magnifying power in a well-developed spectrum, are resolved into a number of fine lines very close together. There are two more groups of lines which are particularly conspicuous, one denoted by *a*, consisting of eight fine lines in the red between A and B, and another *b* in the green near E, consisting of three fine lines, the two stronger of which are separated by a bright space.

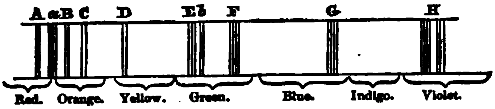
These dark lines show that the solar spectrum is not continuous; in other words, that there do not exist rays of all degrees of refrangibility between the red and the violet.

The aspect, order, and relative distances of the lines in the solar spectrum remain the same, for a prism of given substance, whatever may be the magnitude of its refracting angle; but if the substance of the prism be changed, the relative distances of the fixed lines and the relative widths of the several coloured spaces are likewise altered.

To obtain the lines of the spectrum well developed, it is necessary to use a prism of very uniform substance, free from striæ, and having a refracting angle large enough to yield a very pure and extended spectrum. Prisms for the purpose are generally made of flint glass or rock-crystal, substances having a high dispersive power, that is to say, the power of refracting the red and violet rays in very different degrees (p. 623). A hollow prism filled with sulphide of carbon is also well adapted for the purpose, as it is sure to be uniform, if preserved from variations of temperature, and its dispersive power is very great. To form the spectrum, the sun's rays, or the diffused light of the sky, entering a darkened room through a narrow slit, or condensed by a cylindrical lens, are made to pass through the prism, and the dispersed beam of light is viewed through an achromatic telescope. The lines and intermediate spaces are thereby magnified, the number seen being greater in proportion to the magnifying power of the telescope. The most favourable position for the prism is that of minimum deviation.

Lines also exist beyond A in the red, and beyond the violet in a space occupied by very faint lavender-coloured rays. The first were observed by **Brewster** in a space equal to AB (*fig.* 667), the second by Sir **John Herschel**. To render these lines visible, several precautions are required; amongst others it is necessary to intercept all the rays between the red and violet, and line the tube of the telescope with black velvet. By adopting these and other precautions, and using a prism of oil of cassia, which possesses a high dispersive power, **Brewster** was able to distinguish altogether about 1000 lines in the spectrum, a map of which, together with a delineation of the two extremities of the solar spectrum, as observed by **Gladstone** when the sun was at about his greatest altitude, is given with a paper "On the Lines of the Solar Spectrum" by **Brewster** and **Gladstone**, published in the Philosophical Transactions for 1860, p. 149.

Fig. 667.



A still greater development of the spectrum, and an increased number of lines, are obtained by passing the rays through a series of prisms. In this manner **Kirchoff** has observed about 2000 lines, and has been enabled to lay down a very elaborate map of the solar spectrum, which is published in his work, translated by Roscoe, under the title—*Researches on the Solar Spectrum, and on the Spectra of the Chemical Elements.*

Gassiot has constructed a train of nine flint glass prisms with angles of 45°, and another of eleven sulphide-of-carbon prisms with angles of 45°, with which further observations have been made. (Proc. Roy. Soc. xii. 536; xiii. 183.)

Solar light reflected from a white surface, also that of the clouds, and that of the moon and planets, give spectra exhibiting the same principal lines, and disposed in the same order, as in the spectrum formed by the direct rays of the sun. In the spectra of Mars, Jupiter, and Venus, the lines D, E, F may be very clearly distinguished. But the fixed stars give spectra containing different lines. That of *Sirius* contains two dark lines in the blue, and one very strong line in the green, but none in the yellow or orange; that of *Pollux* contains several faint lines, the line D occupying apparently the same place as in the solar spectrum. See further a paper by **Huggins** and **Miller**. (Proc. Roy. Soc. xiii. 64.)

Effect of coloured Gases on the appearance of the Lines. When a ray of light passes through a coloured gas before falling on the prism, dark lines make their appearance due to the absorption of certain rays by the gas. When the light of a lamp, which of itself gives a spectrum containing only bright lines (p. 622), is passed through the red vapour of pernitric oxide, the violet and blue portions of the spectrum are covered with black lines or rather bands, which become broader as the density of the gas is increased, and ultimately join, so as completely to obliterate the violet rays; at the same time dark lines make their appearance in the yellow, and ultimately extend into the red (**Brewster**, Phil. Mag. [3], viii. 384). Iodine- and bromine-vapours produce dark lines different from those formed by pernitric oxide, appearing first in the green and yellow, then in the orange, and at the commencement of the red, some being quite black while others formed dark bands. The mere existence of colour in a vapour does not, however, necessitate the existence of bands in its spectrum. The red vapours of chloride of tungsten, for example, give no lines whatever. Neither can the position of the lines be inferred from the colour of the gas; with green perchloride of manganese, they are most abundant in the green, while with the red vapours of pernitric oxide, they increase in depth and number as they approach the violet. The vapours of simple bodies as well as of compounds may produce lines, and two simple bodies which singly do not produce them, may produce them abundantly in their compounds; *e.g.*, neither oxygen, nitrogen, nor chlorine, when uncombined, produces lines, but some of the oxides, both of nitrogen and chlorine, exhibit the phenomena in the most striking manner. There are, however, oxides both of nitrogen and chlorine, some of them coloured, which do not occasion the appearance of lines. Lines may also be produced by simple substances, which disappear in their compounds; thus iodine produces lines which do not appear in the spectrum of hydriodic acid. Sometimes the same lines are produced by different degrees of oxidation of the same substance, a remarkable instance of which is afforded by the oxides of chlorine. (W. A. **Miller**, *Elements of Chemistry*, 3rd ed. i. 164.)

When solar light is passed through a coloured vapour, the density of which is gradually increased, absorption-bands make their appearance, faint at first and easily distinguished, but gradually becoming blacker, and ultimately obliterating the ordinary lines. The two systems of lines are in fact distinct in the spectra of all coloured vapours, excepting that of pernitric oxide, in which they coincide. (**Brewster**.)

As the atmosphere possesses a slight colour, it is possible that some at least of the ordinary lines of the solar spectrum may be due to the absorption of certain rays during their passage through the earth's atmosphere; and in fact the lines are more numerous, and some of them, especially those in the red, are remarkably distinct when the sun is near the horizon, and its rays have consequently to travel through a greater thickness of atmospheric air, than when he is at a greater altitude; but the greater number of the lines are probably due to another cause, to be considered hereafter. (Brewster and Gladstone, Phil. Trans. 1860, p. 149; Gladstone, Proc. Roy. Soc. xi. 305.)

Spectra of Flames and Incandescent bodies.

Incandescent solids and liquids give continuous spectra without any dark lines or spaces. Flames, *i.e.*, incandescent gases or vapours, give spectra consisting of bright bands, more or less numerous, with dark spaces between. An alcohol flame or that of a Bunsen's burner in which common salt or other volatile sodium-compound is ignited, gives a spectrum reduced to a narrow yellow band, coincident with the solar line D. Lithium ignited in a similar manner exhibits a single bright crimson line near the solar C. The potassium-spectrum, similarly produced, consists of a red band coinciding with A, and a violet band not coinciding with any of the principal solar lines, the intermediate portion of the spectrum being filled up with a diffused light. The thallium spectrum consists of an intense green line near the solar line E, which is split up by Gassiot's train of eleven sulphide-of-carbon prisms into three separate lines. The spectra of the alkaline earths are equally definite, though more complicated. (See ANALYSIS, INORGANIC; also SPECTRAL ANALYSIS.)

In some cases, new series of bands become visible as the temperature rises; thus the spectrum of chloride of lithium in the flame of a Bunsen burner, gives but a single intense crimson line; in a hotter flame, as that of hydrogen, it gives an additional orange ray; and in the oxy-hydrogen jet and in the voltaic arc, a broad brilliant blue band likewise comes out. A similar effect is perceived in the case of metallic iron, of thallium, and other metals when heated by the voltaic arc. A. Mitscherlich (Pogg. Ann. cxvi. 499) has shown that in flames of low temperature, the lines produced vary with the compound employed, the spectrum then observed being that due to the compound, and not to its elementary constituents; the spectrum of copper, for example, differs considerably from that of an alcoholic solution of chloride of copper, while that from an alcoholic solution of iodide of copper differs from both.

Spectra of the Electric Light.—The spectrum of the electric light exhibits bright lines like those of flames. This was first observed by Wollaston, afterwards by Fraunhofer, who found that the line of bluish light obtained by discharging the electricity of a machine through a very fine wire, gave a spectrum containing a very bright line in the green. Wheatstone has shown that the electric light from the voltaic battery, the ordinary electric machine, and the induction coil, yield the same spectra when the spark passes between conductors of the same kind; but the number and position of the lines varies with the nature of the metallic poles; if they are formed of an alloy, two systems of lines are obtained, one belonging to each of the metals; the same is also the case when the two poles are formed of different metals. These facts show plainly that the electric spark contains particles of metal detached from the conductors between which it passes.

Masson, in the course of his researches on electric photometry, already cited (p. 596), examined the spectra produced by various metals when employed as dischargers to a Leyden jar, and when heated by the voltaic arc, and found them to contain a much greater number of lines than those of the same metals delineated by Wheatstone. The difference was subsequently explained by Angström (Phil. Mag. 1855, p. 329), who showed that Masson, in consequence of the intense heat of the electric discharges which he employed, obtained two spectra, one due to the metal, the other to the atmosphere itself, which became ignited. Certain lines observed by Masson as common to the spectra of all the metals, were really those atmospheric lines. By causing the spark to pass between the same metals immersed in various gases, the particular lines due to the metal remained unaltered, whilst the others due to the gaseous medium, disappeared and were replaced by new lines.

For further details, and for the methods of examining the spectra of flames and incandescent bodies, see SPECTRAL ANALYSIS.

Kirchhoff's theory of the Lines in the Solar Spectrum. The vapour of any substance absorbs rays of the same degree of refrangibility as those which are emitted by the same substance in the state of incandescence, that is to say, those which form the bright lines of its spectrum. Thus ignited sodium emits a yellow light, the spectrum of which consists of two bright bands coincident with the double line D of the solar spectrum. If now, through a flame coloured by sodium, the light of lime ignited in the oxy-hydrogen flame, or that of the voltaic arc between carbon-points, be transmitted, the continuous spectrum produced by either of these sources is interrupted by a black line coinciding with the solar line D. In like manner the spectra of potassium, lithium, barium, strontium and copper, may be *reversed*. On these facts Kirchhoff founds an explanation of Fraunhofer's lines. He supposes that the luminous atmosphere, or *photosphere*, of the sun contains the vapours of various metals, and that behind this incandescent atmosphere is the still more intensely heated solid or liquid nucleus of the sun, which emits light of all degrees of refrangibility, and would produce a continuous spectrum, were it not that some of the rays, in passing through the photosphere, are absorbed by vapours which are themselves capable of emitting rays of the same degree of refrangibility, so that Fraunhofer's lines are only the reversed bright lines which would be visible if the more intensely heated nucleus were not there. A very careful comparison of the solar spectrum with those of various metals, has shown that the former contains dark lines coincident with certain bright lines in the spectra of sodium, potassium, magnesium, calcium, iron, chromium, and nickel: hence Kirchhoff infers that the solar atmosphere contains these metals, and possibly also zinc, cobalt, and manganese, but not lithium, copper, or silver. Angström is of opinion that the presence of hydrogen and aluminium may also be considered as proved, and that barium and strontium are probably also present. (See Kirchhoff's *Researches on the Solar Spectrum and on the Spectra of the Chemical Elements*, translated by Roscoe; also the article SPECTRAL ANALYSIS in this Dictionary.)

Dispersive Powers of different Media.

The separation of the extreme rays of the spectrum, and consequently the length of the spectrum produced by different media, exhibits great diversity. Suppose three prisms to be formed, one of water, the second of crown-glass, and the third of flint-glass, with such refracting angles as to produce equal deviations for any given ray of the spectrum, say the line F, about the middle: then it will be found that the crown-glass spectrum is about 1½, and the flint-glass spectrum 3½ times as long as the water spectrum. It appears then that flint-glass disperses the different coloured rays much more than crown-glass, and crown-glass much more than water.

It is this difference in the dispersion produced by different media for the same amount of refraction of a given ray, which renders it possible to form achromatic combinations of prisms and lenses. The object of such combinations is to reproduce white light by recombining the coloured rays which have suffered dispersion; and this is effected by passing the rays which have been dispersed by one lens or prism through a second lens or prism which refracts them the contrary way (see *fig.* 665, p. 619). But it is evident that if all refracting media dispersed the rays equally for a given amount of mean refraction, the only way of effecting this would be to give the two prisms the same refracting angle (see *fig.* 665), or the two lenses (one convex, and the other concave) equal curvatures; but in this case all the rays would be brought back to the same degree of convergence or divergence as they had before passing through the first lens or prism; indeed the combination would act just like a plate of glass with parallel faces, and would produce no alteration in the direction of the rays. But suppose two prisms, the first of crown- and the second of flint-glass, to be placed together as in *fig.* 665, and their refracting angles to be so proportioned as to produce equal deviations of the middle ray of the spectrum; then, as already observed, the flint prism will disperse the rays about twice as much as the crown; and if instead of this, the refracting angles are so adjusted as to produce equal amounts of dispersion, or spectra of the same length, then the angle of the second must be of such a magnitude as to deviate the mean ray less than the crown-glass prism does. Such a combination will recombine the coloured rays and reproduce white light, without bringing back the rays to their original direction. In like manner, if a concave lens of flint-glass be placed behind a convex lens of crown-glass, its curvature may be so adjusted as to recombine the colours without destroying the convergence of the rays produced by the crown-glass lens.

The difference between the indices of refraction of the extreme rays of the spectrum $\mu_v - \mu_r$, or more precisely of the fixed lines B and H, produced by any refracting medium is called the coefficient of dispersion, or simply the dispersion of that medium.

The following is a list of thirteen substances placed in the order of their coefficients of dispersion, as determined by Wollaston, the most dispersive being placed first; *Sulphur, oil of sassafras, flint-glass, oil of turpentine, Iceland-spar, diamond, crown-glass, water, sulphuric acid, alcohol, heavy-spar, rock-crystal, fluor-spar.* The most dispersive of all known liquids is melted phosphorus, then a solution of phosphorus in sulphide of carbon, then sulphide of carbon itself (see p. 629).

The term partial dispersion is applied to the difference of the refractive indices of any other two colours, the red and yellow, blue and green, &c., always referred to the principal fixed line belonging to each colour. The partial dispersions of any two substances are by no means proportional to their total dispersions; consequently the colours are not distributed in the same manner in the spectra formed by the two substances.

Sulphuric acid and oil of cassia, for example, produce spectra of nearly equal lengths; but in the oil of cassia spectrum, the least refrangible portion—namely, the red, orange and yellow—is much less, and the more refrangible portion, from blue to violet, is much more expanded than in that produced by sulphuric acid. In like manner, flint-glass contracts the less, and expands the more refrangible portion of the spectrum, to a greater extent than crown-glass. This irrationality of dispersion must of course be attended to in the formation of achromatic combinations.

The ratio of dispersion of two media is the ratio of the coefficients of dispersion, $\frac{\mu_v - \mu_r}{\mu'_v - \mu'_r}$, or of the partial coefficients belonging to the corresponding fixed lines in the two spectra. This ratio has different values according to the two lines which are considered.

The term dispersive power is applied to the ratio of the dispersion-coefficient to the index of refraction of the mean ray diminished by 1. Taking as the mean ray the line E in the yellow, and calling its index of refraction μ_y, the dispersive power is expressed by the formula, $\frac{\mu_v - \mu_r}{\mu_y - 1}$.

The following table contains the refractive indices of several media for the principal lines of the spectrum, as determined by Fraunhofer; the last column contains the coefficients of dispersion between the lines B and H:

Refracting substances.	B.	C.	D.	E.	F.	G.	H.	Coefficients of dispersion, $\mu_H - \mu_B$
Flint-glass, No. 13 . .	1·62775	1·62968	1·63503	1·64202	1·64826	1·66028	1·67106	0·04331
Crown-glass, No. 9 . .	1·52583	1·52685	1·52958	1·53300	1·53605	1·54165	1·54656	0·02073
Water	1·33093	1·33171	1·33358	1·33585	1·33782	1·34129	1·34418	0·01325
Solution of potash . . .	1·39963	1·40061	1·40280	1·40563	1·40808	1·41258	1·41637	0·01674
Oil of turpentine . . .	1·47049	1·47153	1·47443	1·47835	1·48173	1·48820	1·49387	0·02338
Flint-glass, No. 3 . . .	1·60204	1·60380	1·60849	1·61453	1·62004	1·63077	1·64037	0·03833
„ No. 30 . . .	1·62357	1·62547	1·63058	1·63735	1·64346	1·65540	1·66607	0·04250
Crown-glass, No. 13 . .	1·52431	1·52530	1·52798	1·53137	1·53434	1·53991	1·54468	0·02037
„ letter M . .	1·55477	1·55593	1·55907	1·56351	1·56674	1·57353	1·57947	0·02470
Flint-glass, No. 23 . . .	1·62659	1·62847	1·63367	1·64049	1·64675	1·65885	1·66968	0·43090

Babinet has given a method of measuring the dispersions of bodies which can only be procured in small fragments. The substance being cut into the form of a prism, and its angle measured, a spectrum projected on a screen by a prism of known angle, is viewed through the small prism whose dispersion is to be determined, in such a manner as to recompose the colours (p. 619), the observer gradually increasing his distance from the spectrum till he sees nothing but white light. If the prisms are in the position of least deviation, and their angles are not too large, their dispersions are to one another in the inverse ratio of their distances from the screen.

Gladstone and Dale have made an extensive series of researches on the refraction, dispersion, and sensitiveness of liquids, the last term being used to signify the relation between the change of refraction and the change of volume by heat. The following are the principal results obtained:

1. *Both refraction and dispersion diminish as the temperature increases.* This law has been verified by observations on about 90 liquids (see p. 626).

The following table exhibits these results in the case of a highly dispersive liquid; it will be observed that the sensitiveness of the rays increases in the order of their refrangibility.

Refractive Indices of Sulphide of Carbon for the several Fixed Lines.

Temperature.	Refractive Iudices.						
	A.	B.	D.	E.	F.	G.	H.
11° 36·5	1·6142 1·5945	1·6207 1·6004	1·6333 1·6120	1·6465 1·6248	1·6584 1·6362	1·6386 1·6600	1·7090 1·6827
Difference .	0·0197	0·0203	0·0213	0·0217	0·0222	0·0236	0·0263

On comparing the change of refraction by heat with the corresponding change of volume in sulphide of carbon, water, methylic, ethylic, and amylic alcohols, acetone, acetic acid, formic, acetic, and butyric ethers, methylic and ethylic iodides, salicylate of methyl, bromoform, benzene, xylene, cumene, nitrobenzene, hydrate of phenyl, the rectified oils of turpentine and Portugal, and eugenic acid, it was found that the refractive index minus unity ($\mu - 1$), multiplied into the volume, gives very nearly a constant product at different temperatures. The quantity $\mu - 1$ is termed by the authors, the refractive energy of a substance, and this multiplied into the volume, or divided by the density, is termed the specific refractive energy. The preceding law may then be stated as follows:—*The refractive energy of a body varies directly with its density, under the influence of change of temperature; or in other words, the specific refractive energy of a liquid is a constant not affected by temperature.* The influence of dispersion, however, renders this law not absolutely accurate in the observed numbers: for the change of dispersion does not follow the same law, the spectrum contracting in some cases much more, and in other cases much less rapidly as the volume increases; indeed no relation is as yet discoverable between change of dispersion and density.

2. The results obtained with mixed liquids, appear to show that *the specific refractive energy of a mixture is the mean of the specific refractive energies of its components.* This law was tested with sulphide of carbon and ether, substances which are almost at the opposite limits of the scale, and were found to mix without condensation; also with aniline and alcohol, on mixing which, however, some diminution of volume occurs. In both these cases, the experimental numbers were slightly below those deduced from the mean of the specific refractive energies; yet no other formula could be devised which would give a nearer approximation to the indices actually observed.

3. *Compounds belonging to the same homologous series exhibit a progressive change in refraction and dispersion as they advance in the series; but the deviation and extent of those changes depend on the other substances with which the radicle is combined. If, however, we regard, not the actual indices, but these minus unity divided by the specific gravity, we find an invariable increase as the series advances.*

The following tables exhibit this with regard to various groups of compounds containing the alcohol-radicles, C^nH^{2n+1}.

Specific Refractive Energy.

Radicle.	Alcohol	Iodide.	Ether of acid.	Formate.	Acetate.	Butyrate.	Oxalate.	Mercury-compound.	Stannic compound.	Hydride.
Methyl . . CH^3	·4105	·2359	·3905	. .	. .	. .	. .	·1707	·3727	
Ethyl . . C^2H^5	·4482	·2614	·4127	·3905	·4152	·4402	·3502	·2112	·3876	
Trityl . . C^3H^7	. .	. .	·4333							
Tetryl . . C^4H^9	. .	. .	·4402							
Amyl . . C^5H^{11}	·4896	·3213	·4492	·4432	·4506	·4724	·4306			
Heptyl . . C^7H^{15}	. .	. .	·4750	. .	. .	. .	. .	. .	. .	·5499
Octyl . . C^8H^{17}	·5096	. .	. .	. .	. .	. .	. .	. .	. .	·5522
Dodecatyl $C^{12}H^{25}$	. .	. .	·4890							

Specific Dispersion.

	Alcohol.	Iodide.	Ether of acid.	Acetate.	Mercury-compound.	Stannic compound.	Hydride.
Methyl. CH^3	163	209	168	. .	140	256	
Ethyl . C^2H^5	190	218	178	178	170	268	
Trityl . C^3H^7	. .	235	191				
Tetryl . C^4H^9	. .	. .	191				
Amyl . C^5H^{11}	212	224	198	198			
Heptyl . C^7H^{15}	. .	. .	. .	. .	. .	. .	242
Octyl . C^8H^{17}	237	. .	. .	. .	. .	. .	236

With regard to other groups of homologous bodies, it was found that benzene, benzylene, xylene, cumene and cymene, gave nearly the same numbers, and no regular progressions. Pyridine, picoline, lutidine, and collidine showed an augmentation of the specific refractive energy, but a diminution of the specific dispersion with the advancing series: chinoline and lepidine (the most refractive organic liquid known) showed an increase of each of the optical properties by addition of CH^2. Hence it appears that the influence of the added increment on the rays of light differs in different groups, just as it does in respect to the boiling point.

4. *Isomeric bodies are sometimes widely different in their optical properties: but in many cases, especially where there is close chemical relationship, there is identity also in this respect.* Several hydrocarbons of the type $C^{10}H^{16}$, from essential oils, appear to be identical in actual refractive power, notwithstanding slight differences of density. In dispersion there are some variations, but not in sensitiveness. Other hydrocarbons, however, of the same ultimate composition, but differing considerably in physical properties differ also optically. Metameric compound ethers, such as valerate of ethyl and acetate of amyl, are optically identical. Aniline and picoline, each empirically C^6H^7N, are totally different.

5. *Effect of Chemical Substitution.*—When hydrogen is replaced by some other body, there is generally an increase of the actual refraction and dispersion; but this is due to the increased weight, hydrogen having a very low actual, but a very high specific influence on the rays of light. When two substitution-products are formed by substitution of the same element in a given compound, *e.g.* mono- and tri-chlorobenzene from benzene, the lower one always retains, in its optical properties, a position intermediate between the original substance and the higher product.

From these facts, it may be inferred, as approximately, if not absolutely, true, that: *Every liquid has a specific refractive energy composed of the specific refractive energies of its component elements, modified by the manner of combination, but unaffected by change of temperature; and this refractive energy accompanies it when mixed with other liquids.* The product of the specific refractive energy and the density at any given temperature, is, when added to unity, the refractive index.

The following tables exhibit the numerical results from which the preceding conclusions are deduced.

Table A.

Refractive indices of the lines A, D, H at different temperatures.

The sign ? attached to a liquid denotes that the purity of the specimen is doubted.
An asterisk * attached to a degree of temperature signifies that the observations at that temperature were made on a different occasion to the observations at other temperatures.
Specific gravities not determined from the specimens examined are included in brackets.

No.	Liquid.	Specific gravity.	Temperature of observation.	Refractive indices.		
				A.	D.	H.
1.	Methylic alcohol . . .	0·7972 at 20°C.	20°	1·3264	1·3299	1·3395
			37	1·3205	1·3238	1·3330
2.	Ditto from oxalate . .	0·7960 at 20	20	1·3268	1·3297	1·3396
			29·5	1·3230	1·3262	1·3359
3.	Amylic alcohol . . .	0·8179 at 15·5	24·5	1·3988	1·4030	1·4161
			41	1·3924	1·3966	1·4093
4.	Caprylic alcohol . . .	0·8214 at 15·5	27	1·4157	1·4202	1·4351
			47	1·4073	1·4118	1·4266
5.	Iodide of methyl . .	2·1912 at 20	23·5	1·5203	1·5307	1·5670
			29·5	1·5104	1·5202	1·5549
6.	Iodide of ethyl . . .	1·9228 at 20	23·5	1·5003	1·5095	1·5420
			36	1·4918	1·5006	1·5326
			48	1·4841	1·4934	1·5250
7.	Iodide of trityl . . .	1·7117 at 20	8·5	1·5001	1·5095	1·5418
			20	1·4934	1·5024	1·5342
			30	1·4871	1·4963	1·5272
8.	Iodide of amyl . . .	1·4950 at 20	17·5	1·4816	1·4892	1·5149
			37	1·4720	1·4797	1·5046
9.	Formic ether . . .	0·9088 at 20	22	1·3540	1·3582	1·3694
			31	1·3500	1·3540	1·3652
			40	1·3456	1·3494	1·3608
10.	Acetic ether . . .	0·8648 at 20	20	1·3645	1·3685	1·3798
			28	1·3606	1·3644	1·3755
11.	Acetic ether . . .	0·8972 at 20	23·5	1·3653	1·3692	1·3809
			33	1·3606	1·3643	1·3757
			41	1·3563	1·3602	1·3711
12.	Propionic ether . . .	0·8555 at 20	22·5	1·3696	1·3736	1·3860
			32	1·3657	1·3698	1·3819
			42	1·3610	1·3651	1·3771

TABLE A—*continued.*

No.	Liquid.	Specific gravity.	Temperature of observation.	Refractive indices.		
				A.	D.	H.
13.	Butyric ether	0·8778 at 20°C.	23	1·3850	1·3888	1·4018
			40	1·3768	1·3808	1·3933
14.	Valerianic ether	0·8680 at 20	18	1·3916	1·3958	1·4089
			32·5	1·3856	1·3898	1·4024
15.	Acetate of amyl	0·8680 at 20	24·5	1·3910	1·3950	1·4081
			34·5	1·3867	1·3905	1·4037
			44	1·3817	1·3859	1·3985
16.	Ditto, second specimen	. .	8·5	1·3944	1·3988	1·4113
			21·5	1·3886	1·3928	1·4058
			35	1·3820	1·3866	1·3990
17.	Acetate of octyl?	. .	27·5	1·4045	1·4092	1·4255
			40	1·3972	1·4020	1·4181
18.	Hydride of heptyl	0·7090 at 20	9·5	1·3956	1·3996	1·4135
			22	1·3888	1·3931	1·4059
			36	1·3811	1·3854	1·3976
19.	Hydride of octyl	0·7191 at 20	9	1·4022	1·4065	1·4197
			28·5	1·3931	1·3972	1·4097
			41	1·3870	1·3911	1·4032
20.	Mercuric methyl?	(3·069)	8·5*	1·5274	1·5378	1·5726
			15·5*	1·5262	1·5355	1·5694
			26·5	1·5197	1·5296	1·5626
21.	Mercuric ethyl?	(2·444)	8·5*	1·5300	1·5397	1·5729
			24·5	1·5124	1·5217	1·5538
22.	Stannic ethyl-methyl?	1·2220 at 20	19	1·4555	1·4625	1·4868
			34·5	1·4479	1·4747	1·4783
23.	Stannic ethyl?	1·1920 at 20	23	1·4606	1·4673	1·4905
			35	1·4551	1·4621	1·4844
			48	1·4481	1·4549	1·4769
24.	Triethylarsine	. .	19·5	1·4598	1·4669	1·4919
			26·5	1·4588	1·4657	1·4906
25.	Acetic acid	1·0592 at 20	24	1·3674	1·3718	1·3846
			34·5	1·3635	1·3680	1·3808
			45	1·3596	1·3634	1·3757
26.	Acetone	0·8117 at 15·5	25·5	1·3540	1·3580	1·3706
			40	1·3469	1·3512	1·3631
27.	Amylene	0·7151 at 20	23	1·3832	1·3878	1·4028
			35	1·3786	1·3834	1·3982
28.	Carbonic ether	0·9720 at 20	22	1·3773	1·3810	1·3936
			31	1·3746	1·3787	1·3898
			40	1·3692	1·3734	1·3846
29.	Boracic ether	0·8760 at 20	22·5	1·3664	1·3698	1·3815
			40·5	1·3578	1·3604	1·3724
30.	Silicic ether	0·9320 at 20	20	1·3781	1·3821	1·3940
			33·5	1·3724	1·3768	1·3881
31.	Salicylate of methyl	1·1760 at 20	21	1·5206	1·5319	1·5810
			37	1·5140	1·5253	1·5735
32.	Nitrate of amyl	1·0008 at 20	10	1·4109	1·4157	1·4320
			22·5	1·4053	1·4097	1·4256
			36·5	1·3988	1·4035	1·4191
33.	Chloroform	1·4980 at 20	18	1·4411	1·4463	1·4630
			30	1·4346	1·4397	1·4561
			44	1·4253	1·4308	1·4471
34.	Bromoform	2·6360 at 12	15·5	1·5579	1·5674	1·5998
			29	1·5505	1·5598	1·5921
			39	1·5437	1·5531	1·5846
35.	Dutch liquid	. .	21	1·4175	1·4221	1·4371
			38	1·4082	1·4126	1·4276
36.	Dibromide of bromethylene	2·6160 at 20	18	1·5819	1·5915	1·6249
			39·5	1·5701	1·5787	1·6112
37.	Dibromide of chlorethylene	2·2477 at 20	13	1·5477	1·5559	1·5839
			24	1·5413	1·5494	1·5770

TABLE A—*continued.*

No.	Liquid.	Specific gravity.	Temperature of observation.	Refractive indices.		
				A.	D.	H.
38.	Dichloride of chlorethylene .	1·4177 at 20°C.	13	1·4661	1·4714	1·4892
			29·5	1·4563	1·4619	1·4789
39.	Benzene	0·8667 at 20	10·5	1·4879	1·4975	1·5305
			23	1·4806	1·4900	1·5225
			39	1·4703	1·4793	1·5108
40.	Parabenzene . . .	0·8469 at 20	20	1·4814	1·4903	1·5216
41.	Benzylene	0·8650 at 20	25·5	1·4709	1·4794	1·5090
			32·5	1·4672	1·4755	1·5048
			39	1·4629	1·4710	1·5001
42.	Parabenzylene . . .	0·8333 at 20	28	1·4667	1·4751	1·5030
			40	1·4590	1·4671	1·4944
43.	Benzylene	0·8658 at 20	14	1·4869	1·4957	1·5271
			33	. .	1·4856	
44.	Xylene	0·8660 at 20	11	1·4888	1·4982	1·5300
			28	1·4788	1·4879	1·5192
			42	1·4716	1·4805	1·5166
45.	Cumene (from cuminic acid)	0·8710 at 20	7	1·4898	1·4983	1·5280
			27·5	1·4783	1·4864	1·5148
46.	Cumene (from impure wood-spirit) . . .	0·8580 at 20	8·5	1·4687	1·4759	1·5008
			24	1·4608	1·4680	1·4919
			34	1·4555	1·4634	1·4848
47.	Pseudocumene . . .	0·8692 at 20	12·5	1·4843	1·4932	1·5236
			35·5	1·4728	1·4812	1·5093
48.	Cymene	0·8610 at 20	8	1·4760	1·4834	1·5076
			29	1·4648	1·4717	1·4957
49.	Cymene (from camphor) .	0·8565 at 20	12	1·4731	1·4803	1·5050
			26	1·4659	1·4729	1·4975
			36	1·4614	1·4684	1·4927
50.	Chlorobenzene . . .	1·1080 at 20	9	1·5194	1·5290	1·5636
			27·5	1·5095	1·5189	1·5528
51.	Trichlorobenzene . .	1·4500 at 20	20	1·5563	1·5671	1·6065
			37	1·5495	1·5600	1·5983
52.	Nitrobenzene . . .	1·1590 at 20	25	1·5331	1·5465	1·5832G.
			38	1·5266	1·5399	1·5766G.
53.	Dinitrobenzene in 2 equivs. of nitrobenzene .	1·2670 at 20	23·5	1·5460	1·5600	1·5994G.
			35	1·5404	1·5542	1·5932G.
			56	1·5296	1·5425	1·5816G.
54.	Aniline	1·0270 at 16	21·5	1·5644	1·5784	1·6297
			37	1·5567	1·5701	
			42	1·5537	1·5676	1·6183
			47	1·5520	1·5647	1·6145
55.	Amyl-aniline . . .	0·9177 at 20	23·5	1·5114	1·5222	1·5622
			42	1·5035	1·5138	1·5532
56.	Hydrate of cresyl . .	1·0364 at 20	11·5	1·5341	1·5454	1·5824
			32	1·5281	1·5377	1·5733
57.	Pyridine	0·9738 at 20	21·5	1·4940	1·5030	1·5387
			36	1·4860	1·4951	1·5301
58.	Picoline	(0·955)	22·5	1·4188	1·4980	1·5314
			37·5	1·4803	1·4890	1·5213
			52	1·4718	1·4807	1·5122
59.	Lutidine	(0·936)	8·5*	1·4932	1·5028	1·5353
			22·5	1·4894	1·4987	1·5308
60.	Collidine	(0·921)	23·5	1·4927	1·5013	1·5329
			45	1·4820	1·4907	1·5210
61.	Chinoline	(1·0810 at 10)	24	1·5567	1·5687	1·6198
			35	1·5466	1·5587	1·6084
			37	1·5496	1·5616	1·6124
62.	Lepidine	1·0720 at 15	21	1·6039	1·6189	1·6822
			47	1·5909	1·6054	1·6473G.
63.	Hydrocarbon from anise .	0·8580 at 20	11	1·4653	1·4718	1·4921
			30	. .	1·4625	

TABLE A—*continued.*

No.	Liquid.	Specific gravity.	Temperature of observation.	Refractive indices.		
				A.	D.	H.
64.	Hydrocarbon from turpentine	0·8644 at 20° C.	10*	1·4669	1·4734	1·4934
			24	1·4596	1·4653	1·4845
			47	1·4487	1·4545	1·4730
65.	„ „ carraway	0·8529 at 20	14	1·4640	1·4701	1·4901
			37	1·4529	1·4589	1·4783
66.	„ „ thyme .	0·8635 at 20	25	1·4594	1·4652	1·4856
			35·5	1·4545	1·4606	1·4805
67.	„ „ bay .	0·8510 at 20	23	1·4545	1·4610	1·4818
			43	1·4468	1·4528	
68.	„ „ bergamot	0·8467 at 20	26·5	1·4574	1·4640	1·4865
			38	1·4517	1·4578	1·4800
69.	„ „ cloves .	0·9041 at 20	17	1·4918	1·4985	1·5209
			28·5	1·4870	1·4936	1·5157
			39	1·4828	1·4892	1·5110
70.	„ „ cubebs .	0·9270 at 20	10·5	1·4988	1·5055	1·5294
			20	1·4950	1·5014	1·5252
			31	1·4905	1·4977	1·5209
71.	Carvene	0·9530 at 20	12·5	1·4913	1·4992	1·5270
			24·5	1·4862	1·4935	1·5196
			34	1·4812	1·4884	1·5145
72.	Eugenic acid . . .	1·0640 at 20	18	1·5285	1·5394	1·5780
			27·5	1·5244	1·5347	1·5722
73.	Camphor of peppermint .	0·8786 at 43	30	1·4503	1·4553	1·4703
			43	1·4451	1·4505	1·4653
74.	Glycerin	1·2610 at 17	20	1·4659	1·4705	1·4850
			30	1·4634	1·4680	1·4823
			48	1·4586	1·4631	1·4773
75.	Nitroglycerin? . . .	(1·60)	13·5	1·4683	1·4749	1·4947
			32·5	1·4596	1·4662	
76.	Nicotine	1·0260 at 18	18	1·5149	1·5234	1·5542
			32	1·5107	1·5194	1·5493
77.	Tribromide of phosphorus .	2·880 at 20	25	1·6698	1·6866	1·7506
			36	1·6627	1·6792	1·7422
78.	Trichloride of phosphorus .	1·4530 at 20	25·5	1·5030	1·5118	1·5418
			38	1·4957	1·5042	1·5334
79.	Oxychloride of phosphorus .	1·6800 at 20	17	1·4810	1·4882	1·5118
			26	1·4756	1·4832	1·5067

TABLE B.

Refractive Indices.

The liquids in this table are arranged according to their power of refracting the line A at 20° C.

Liquid.	Temp.	Refractive indices.							
		A.	B.	C.	D.	E.	F.	G.	H.
Phosphorus . .	35° C.	2·0389	. .	. .	2·0746	. .	2·1201	2·1710	2·2267?
Phosphorus in sulphide of carbon . .	?	1·9209	1·9314	. .	1·9527	1·9744	1·9941	2·0361	2·0746
Tribromide of phosphorus . . .	25	1·6698	1·6752	. .	1·6866	. .	1·7083	1·7300	1·7506
Sulphide of carbon .	11	1·6142	1·6207	1·6240	1·6333	1·6465	1·6584	1·6836	1·7090
Lepidine . . .	21	1·6039	1·6094	. .	1·6189	. .	1·6403	1·6615	1·6822
Dibromide of bromethylene . .	18	1·5819	1·5851	. .	1·5915	. .	1·6037	1·6149	1·6249
Rectified oil of cassia	28	1·5649	1·5699	1·5727	1·5801	1·5909	1·6014	1·6244	
Aniline . . .	21·5	1·5644	1·5684	. .	1·5774	. .	1·5951	1·6125	1·6297
Chinoline . . .	24	1·5567	1·5617	. .	1·5687	. .	1·5879	1·6030	1·6198

Table B—*continued.*

Liquid.	Temp.	Refractive indices.							
		A.	B.	C.	D.	E.	F.	G.	H.
Trichlorobenzene .	20°C.	1·5563	1·5602	. .	1·5671	. .	1·5809	1·5945	1·6065
Bromoform . .	15·5	1·5579	1·5610	1·5628	1·5674	1·5737	1·5790	1·5901	1·5998
Dinitrobenzene in nitrobenzene . .	23·5	1·5460	1·5506	. .	1·5600	. .	1·5791	1·5994	. .
Dibromide of chlorethylene . . .	12·5	1·5472	1·5500	. .	1·5554		1·5659	1·5748	1·5830
Nitrobenzene . .	25	1·5331	1·5374	1·5398	1·5465	1·5554	1·5643	1·5832	. .
Hydrate of phenyl .	13	1·5377	1·5416	1·5433	1·5488	1·5564	1·5639	1·5763	1·5886
Hydrate of cresyl .	11·5	1·5341	1·5377	. .	1·5445	. .	1·5573	1·5699	1·5813
Eugenic acid . .	18	1·5285	1·5321	1·5341	1·5394	1·5464	1·5528	. .	1·5780
Mercuric methyl .	26·5	1·5197	1·5232	. .	1·5296	. .	1·5368	1·5526	1·5626
Salicylate of methyl .	21	1·5206	1·5241	1·5263	1·5319	1·5402	1·5478	1·5640	1·5810
Iodide of methyl .	16	1·5203	1·5234	. .	1·5307	1·5377	1·5440	1·5558	1·5670
Mercuric ethyl . .	8·5	1·5300	1·5333	. .	1·5397	. .	1·5518	1·5634	1·5729
Nicotine . . .	18	1·5149	1·5174	. .	1·5234	. .	1·5346	1·5449	1·5542
Chlorobenzene . .	9	1·5194	1·5223	. .	1·5290	. .	1·5418	1·5530	1·5636
Amyl-aniline . .	23·5	1·5114	1·5150	1·5168	1·5222	1·5292	1·5361	1·5491	1·5622
Trichloride of phosphorus . . .	23·5	1·5052	1·5088	. .	1·5148	. .	1·5252	1·5357	1·5446
Iodide of ethyl . .	23·5	1·5003	1·5034	. .	1·5095	1·5156	1·5214	1·5321	1·5420
Rectified oil of santalwood . . .	25·5	1·4954	1·4977	. .	1·5015	. .	1·5093	1·5161	1·5223
Hydrocarbon from cubebs . . .	10·5	1·4988	1·5012	. .	1·5055	.	1·5145	1·5227	1·5294
Pyridine . . .	21·5	1·4940	1·4967	. .	1·5030	. .	1·5155	1·5278	1·5387
Lutidine . . .	22·5	1·4894	1·4924	. .	1·4987	. .	1·5100	1·5204	1·5308
Collidine . . .	23·5	1·4927	1·4958	. .	1·5018	. .	1·5127	1·5232	1·5329
Hydrocarbon from cloves . . .	17	1·4918	1·4944	. .	1·4985	. .	1·5064	1·5140	1·5209
Pseudocumene . .	12·5	1·4843	1·4872	. .	1·4932	. .	1·5040	1·5146	1·5236
Iodide of amyl . .	17·5	1·4816	1·4843	. .	1·4892	1·4941	1·4987	1·5074	1·5149
Oxychloride of phosphorus . . .	17	1·4810	1·4840	. .	1·4882	. .	1·4967	1·5047	1·5118
Benzene . . .	10·5	1·4879	1·4913	1·4931	1·4975	1·5036	1·5089	1·5202	1·5305
Benzylene . . .	14	1·4869	1·4898	. .	1·4957	. .	1·5072	1·5174	1·5271
Cymene . . .	29	1·4648	1·4671	. .	1·4717	1·4766	1·4808	1·4866	1·4957
Nitroglycerin . .	13·5	1·4683	1·4706	. .	1·4749	. .	1·4824	1·4899	1·4947
Hydrocarbon from Portugal . .	25	1·4617	1·4640	. .	1·4684	. .	1·4758	1·4826	1·4894
Cumene (2nd specimen) . . .	8·5	1·4687	1·4709	. .	1·4759	. .	1·4853	1·4936	1·5008
Stannic ethyl . .	23	1·4606	1·4629	. .	1·4673	. .	1·4758	1·4838	1·4905
Dichloride of chlorethylene . .	13	1·4661	1·4680	. .	1·4714	. .	1·4784	1·4841	1·4892
Hydrocarbon from turpentine . .	24	1·4596	1·4616	. .	1·4653	1·4691	1·4724	1·4790	1·4845
Hydrocarbon from carraway . .	24	1·4594	1·4615	. .	1·4652	. .	1·4724	1·4789	1·4844
Hydrocarbon from bergamot . .	26·5	1·4574	1·4598	. .	1·4640	. .	1·4721	1·4798	1·4865
Rectified oil of citronella . . .	19	1·4598	1·4619	. .	1·4655	. .	1·4730	1·4795	1·4860
Hydrocarbon from bay	23	1·4545	1·4567	. .	1·4610	. .	1·4690	1·4756	1·4818
Stannic ethyl-methyl .	19	1·4555	1·4578	1·4590	1·4625	1·4674	1·4716	1·4795	1·4868
Chloroform . .	10	1·4438	1·4457	1·4466	1·4490	1·4526	1·4555	1·4614	1·4661
Octylic alcohol . .	9·5	1·4230	1·4246	1·4255	1·4279	1·4309	1·4338	1·4386	1·4429
Nitrate of amyl . .	10	1·4109	1·4127	. .	1·4157	. .	1·4219	1·4274	1·4320
Amylic alcohol . .	25	1·3981	1·3999	. .	1·4024	. .	1·4078	1·4122	1·4161
Hydride of octyl .	9	1·4022	1·4037	. .	1·4065	. .	1·4076	1·4141	1·4197
Hydride of heptyl .	9·5	1·3956	1·3968	. .	1·3996	. .	1·4045	1·4087	1·4135

Table B—*continued.*

Liquid.	Temp.	Refractive indices.							
		A.	B.	C.	D.	E.	F.	G.	H.
Acetate of amyl .	8·5° C.	1·3944	1·3958	. .	1·3998	. .	1·4035	1·4077	1·4113
Butyric ether . .	23	1·3850	1·3864	. .	1·3888	. .	1·3938	1·3981	1·4018
Amylene . . .	8	1·3850	1·3866	. .	1·3896	. .	1·3944	1·3992	1·4033
Carbonic ether . .	22	1·3773	1·3785	. .	1·3810	. .	1·3856	1·3896	1·3936
Propionic ether . .	22·5	1·3696	1·3713	. .	1·3736	. .	1·3785	1·3827	1·3860
Boracic ether . .	22·5	1·3664	. .	. .	1·3698	. .	1·3742	1·3785	1·3815
Acetic ether . .	20	1·3645	1·3658	. .	1·3685	. .	1·3728	1·3766	1·3798
Alcohol . . .	15	1·3600	1·3612	1·3621	1·3638	1·3661	1·3683	1·3720	1·3751
Acetone . . .	25·5	1·3540	1·3554	. .	1·3582	. .	1·3629	1·3670	1·3706
Formic ether . .	22	1·3540	1·3553	. .	1·3582	. .	1·3627	1·3666	1·3694
Ether . . .	15	1·3529	1·3545	1·3554	1·3566	1·3590	1·3606	1·3646	1·3683
Water . . .	15	1·3284	1·3300	1·3307	1·3324	1·3347	1·3366	1·3402	1·3431
Methylic alcohol .	20	1·3264	1·3277	. .	1·3299	.	1·3330	1·3669	1·3395

Cause of Dispersion.—As the several colours correspond to vibrations of different rapidity, and the deviation of rays of light in refraction depends on the change of velocity of light in passing from one medium into another, it follows that in order to explain dispersion, we must suppose that this change of velocity is different for rays of different colours, that is to say, that waves of different length travel through refracting media with different velocities. This consequence was for a long time regarded as a grave objection to the undulatory theory of light, being in fact in contradiction to the general formula for the velocity of undulations established by Newton, viz. $v^2 = \frac{e}{d}$. It must, however, be remembered that though the velocity of light in free space is the same for rays of all colours (p. 594), it is by no means necessarily so in transparent media, which retain the ether imprisoned, as it were, between their particles. The waves must then turn round these molecules, and it is easily conceivable that the retardations thus produced may be greater for the shorter than for the longer undulations. That such is the case has in fact been proved by the analytical researches of Cauchy; but the demonstration is not of a character to be introduced into this work, and does not admit of representation in a more elementary form.

Heating, Chemical, and Phosphorogenic Rays of the Spectrum.

All the rays of the solar spectrum are capable of giving heat as well as light. A thermometer held in any part of the spectrum indicates a rise of temperature; but the heating effect is very different in different parts, being greatest at the red end of the spectrum; but the particular position of the maximum heating effect varies with the kind of prism used. Moreover, there are invisible heat-rays situated beyond the red, and therefore of lower refrangibility than any of the luminous rays; and when a flint-glass prism is used, the maximum of heating power is situated beyond the visible red rays.

The spectra of flames exhibit similar results, provided the heat-rays which they emit are capable of passing through the substance of which the prism is formed, which is not always the case. (See Radiation of Heat.)

The solar rays are also capable of producing chemical change, chiefly of the reducing order. Thus silver-salts are blackened and more or less reduced by exposure to daylight, and the leaves of plants, under the influence of sunlight, decompose the carbonic acid in the air, and assimilate its carbon. This action is exerted by all the luminous rays of the spectrum, but chiefly by the violet rays, and by non-luminous rays extending to a considerable distance beyond the violet. The yellow and red rays have but little chemical power: hence ordinary flames (hydrocarbon flames) in which these rays greatly predominate, exert but little action on chloride of silver and other bodies, which change rapidly under the influence of solar light; and in monochromatic yellow flames, such as that of alcohol containing a sodium-salt, the chemical action is altogether imperceptible. Photographers develope their pictures in rooms into which light is admitted only through yellow glass or yellow paper. Violet flames, on the other hand, like that of burning magnesium, emit rays whose chemical activity rivals that of sunlight, though their luminosity is incomparably less. The maximum of chemical action is not, however, produced upon all substances in the same part of the spectrum. According to E. Becquerel (Ann. Ch. Phys. [3], ix. 257), chloride of silver begins to blacken in the extreme violet between the lines H and G, the coloration extending on the one side nearly to F, and on the other considerably beyond the visible violet. With the iodide and bromide of silver, the effect is similar, excepting that the action does not extend so far beyond the violet, and the maximum does not occupy the same place. Guaiac-resin, which is turned blue by exposure to sunlight, is not at all affected by any of the visible rays of the spectrum, the action beginning only in the ultra-violet, and the maximum being situated a long way beyond the end of the visible spectrum.

The chemical spectrum contains fixed lines, that is to say, portions in which no chemical action is produced, so that when a piece of paper covered with chloride of silver or other sensitive substance has been exposed to the spectrum, the blackened surface is traversed by lines of the same colour as the original substance, in the ultra-violet as well as in the visible portion of the spectrum. A diagram of these lines will be given in the next article on the CHEMICAL ACTION OF LIGHT.

The interposition of *colourless plates* or *films* does not modify the chemical action in the visible part of the spectrum between A and H; that of the rays between H and P is likewise unaltered by certain transparent substances, such as water, alcohol, sulphuric acid, &c., whereas other substances, both liquid and solid, weaken the chemical action of the most refrangible chemical rays situated beyond the visible spectrum, from P to a point more or less near to H. With nitric acid and oil of lemons, the absorbent action stops at N; with creasote, bitter almond-oil, and a dilute aqueous solution of sulphate of quinine, at H. (For further details respecting the chemical action of light, see the next article.)

The different rays of the spectrum also differ in their power of producing phosphorescence. When Canton's phosphorus spread on a sheet of paper is exposed in a dark room to the action of the spectrum, phosphorescence is produced by the rays between G and P (see figure in the next article); there is a less luminous portion beween I and N, and two maxima, one between H and G, the other in O. The Bolognian phosphorus gives similar results, excepting that there is no minimum in I N, and only one maximum between I and M. It appears therefore that the phosphorogenic rays occupy the same portion of the spectrum as the chemical rays.

The colour of the phosphorescent light, which may vary from orange-red to violet, has no relation to that of the exciting rays, excepting in the case of three substances: *sulphide of barium*, which shines with an orange-yellow light when it has been exposed to the rays between H and P, with a more reddish light when it receives the blue and violet rays; *sulphide of calcium*, which shines with an orange-red light when it has been exposed to the rays between F and O, and exhibits a slight greenish shade when the incident rays are comprised between O and P; lastly, the substance obtained by the action of sulphide of potassium on oyster-shells calcined with lime, which emits a violet-indigo light after exposure to rays of the same tint, and becomes blue in the ultra-violet rays. In general, the emitted rays are less refrangible than the exciting rays, the last-mentioned substance, however, forming an exception to this rule.

The *electric light*, which is very bright and very rich in highly refrangible rays, produces phosphorescence more actively than the solar rays. The sudden discharge is more efficacious than the continuous light of the voltaic arc.

The phosphorogenic spectrum likewise exhibits dark lines or lines of no action; but to see them it is necessary to extend the spectrum to about ten times its usual length by means of diverging lenses. Dark lines are then seen on the phosphorescent surface, occupying the same position as those of the luminous and chemical spectra. They may be rendered more distinct by heating the phosphorescent body to between 200° and 300°; the luminous portions then become brighter, and the lines more distinct.

Transparent substances, both coloured and colourless, placed in the course of the incident rays, absorb the phosphorogenic rays in the same parts of the spectrum as the luminous and chemical rays.

Identity of the calorific, luminous, chemical, and phosphorogenic rays.—It was formerly supposed that the rays producing these several effects are distinct from each other; in fact, that luminous bodies emit four kinds of rays, which, when dispersed by a prism, form four spectra superposed over each other, but having their maxima and minima at different places. But it is much more probable that the rays or undulations are all of one kind, and capable of producing one or other of the effects above mentioned, according to the nature of the bodies or organs upon which they act. In fact, the calorific and chemical rays are reflected and refracted in the same manner as luminous rays of equal refrangibility; the calorific, luminous, and chemical spectra are interrupted by the same lines; and bodies which absorb the luminous rays likewise absorb heat-rays and chemical rays of the same degree of refrangibility. The same is true with regard to the phosphorogenic rays, so far as they extend into the luminous part of the spectrum. Moreover, Fizeau and Foucault have shown that the chemical actions produced at the focus of a lens by the light of the voltaic arc and the lime-light, are to one another in the same ratio as the luminous intensity.

The production of the several effects above mentioned by the same rays, is quite in accordance with the wave-theory of light. The waves of the ether striking on the surface of ponderable bodies throw their particles into vibration, and the particular effects produced are determined by the rate and mode of vibration thus excited, which themselves depend upon the manner in which the particles of the body are held together, as well as upon the rate of vibration of the incident waves. Rays whose length and rapidity of vibration are such as to excite in our organs the sensations of both heat and light, may, when they impinge upon a ponderable body, set its particles into such a rate of vibration as to excite in the surrounding ether, waves whose length and rapidity of vibration correspond to the least refrangible rays of the spectrum beyond the visible red. In like manner, we shall presently see that the invisible chemical rays at the other end of the spectrum may excite vibrations of less rapidity, which render visible the body on which they impinge. The effect thus produced is called

Fluorescence.

It was observed some years ago, by Sir John Herschel, that a solution of sulphate of quinine, though perfectly colourless by transmitted light, exhibits in certain aspects a peculiar blue colour. This blue light was found to be produced only by a very thin stratum of liquid adjacent to the surface by which the light entered, and the incident beam, after having passed through the stratum from which the blue light came, was not sensibly weakened or coloured, but had lost the power of producing the usual blue colour when admitted into another solution of sulphate of quinine. Light thus modified was said by Sir J. Herschel to be *epipolised.*

Similar phenomena were observed by Sir D. Brewster in an alcoholic solution of chlorophyll, the green colouring matter of leaves, the path of a beam of sunlight admitted into the green solution being marked by a bright light of a blood-red colour. The same appearance was afterwards observed in various vegetable solutions and essential oils, and in some solids. Brewster distinguished this phenomenon by the name of *internal dispersion*, attributing it to the irregular reflection of the light from coloured particles suspended in the liquid, and was of opinion that Herschel's epipolic dispersion was only a particular case of this internal dispersion.

The true explanation of these remarkable phenomena has, however, been given by Professor Stokes, who has shown that the peculiar dispersion produced by sulphate of quinine, and the other liquids above mentioned, is due *to a change of refrangibility in the rays of light.* The following experiment renders this evident:—

A solar spectrum is formed by means of an achromatic lens, and one or more prisms of flint glass, sufficiently pure to render visible the principal fixed lines, and a tube filled with a solution of sulphate of quinine is passed along this spectrum, from the red towards the violet end. Nothing peculiar is observed while the tube is held in the less refrangible part of the spectrum, the light passing through it freely and without sensible modification; but just before it reaches the extremity of the violet, a peculiar blue diffused light makes its appearance at the surface of the fluid by which the light enters, and remains visible, even after the tube has passed beyond the violet into the invisible portion of the spectrum, acquiring, in fact, its greatest intensity at a certain distance beyond the extreme violet.

The stratum of liquid from which the diffused blue light emanates is thinner in proportion as the incident rays are more refrangible; and, from a little beyond the extreme violet to the end of the spectrum, the blue space is reduced to an excessively thin stratum adjacent to the surface by which the rays enter. It appears, therefore, that the solution, though transparent with respect to nearly the whole of the visible rays, is of an inky blackness with respect to the invisible rays more refrangible than the violet. Nevertheless, these rays, when once they have been converted into the visible blue light, pass through the liquid with facility. They must, therefore, be essentially altered in character. Now, a change in the quality of light must consist, either in a modification of its state of polarisation, or in its period of undulation. The former supposition is excluded by the fact that the light thus modified is not polarised at all. It must, therefore, have undergone a change in its rate of vibration, and consequently a change of refrangibility. The existence of this change is, moreover, distinctly proved by examining the diffused light with a prism. It is then found to be by no means homogeneous, but to be resolvable into rays of unequal refrangibility, the whole of which are, however, comprised within the limits of the visible spectrum. *The diffused blue light consists of the chemical rays rendered visible by a change in their refrangibility.*

The diffusion thus produced is entirely distinct from that which is due to reflection from irregularities or suspended particles. The two phenomena are often produced together in the same medium; but they are easily distinguished by the fact that the light diffused by irregular reflection is more or less polarised, whereas the light diffused in the manner above described is entirely unpolarised, even if the incident rays were themselves polarised. This phenomenon, to which Professor Stokes originally gave the name of *true diffusion*, to distinguish it from the false diffusion produced by irregular reflection, is now called FLUORESCENCE.

It is exhibited by many solutions, and by many solid bodies, opaque as well as transparent, the colour of the diffused light varying with the nature of the medium. An aqueous infusion of horse-chesnut bark exhibits it very strongly, producing a blue colour similar to that of sulphate of quinine. Many compounds of sesquioxide of uranium are also highly fluorescent, and diffuse a greenish-blue light, especially the nitrate, and *canary-glass*. A decoction of madder mixed with alum gives a yellow or orange-yellow fluorescence; tincture of turmeric and alcoholic extract of thorn-apple seeds diffuse a greenish light; an alcoholic solution of chlorophyll, a red light.

When the fluorescence is strong, as with sulphate of quinine, it may be seen by merely viewing the substance by ordinary diffused daylight. For more accurate observation and for detecting fluorescence when it exists only in a slight degree, the following method is recommended by Stokes (Phil. Mag. [4], vi. 304):—

Light is admitted into a darkened room through a hole several inches in diameter in the window-shutter, and the object to be examined is placed on a small shelf, blackened at the top, and fixed just below. The hole is covered with an absorbing medium, called the *principal absorbent*, so selected as to transmit only the feebly luminous and invisible rays of high refrangibility. The body on the shelf is viewed through the second medium, the *complementary absorbent*, which is chosen so as to be as transparent as possible to those rays which are absorbed by the first, and to absorb all the rays which are transmitted by the first. If the media are well selected, they produce a very near approach to perfect darkness; and if the object appears unduly luminous, that effect most probably arises from fluorescence. To determine whether the illumination is really due to that cause, the complementary absorbent is removed from before the eyes to the front of the aperture, when the illumination, if really due to fluorescence, almost wholly disappears; whereas, if it be due merely to scattered light capable of passing through both media, it remains. In examining feebly fluorescent substances, however, it is better to keep the second medium in its place before the eye, and to use a third medium, the *transfer-medium*, placing the last alternately in the path of the incident rays, and between the object and the eye. Still greater delicacy of observation is attained by placing the substance side by side with a small white porcelain tablet, which is quite destitute of fluorescence, and examining the two as above. Or, again, the object being placed on the tablet, a slit is held close to it, in such a position as to be seen projected partly on the object, partly on the tablet, and the slit is viewed through a prism. The fluorescence of the object is evidenced by light appearing in regions of the spectrum, in which the rays coming through the principal absorbent, and scattered by the tablet, then produce nothing but darkness. These methods are delicate enough to show the fluorescence of white paper, even on a very gloomy day.

It is not merely the most refrangible rays that are capable of producing fluorescence; the rays of any part of the spectrum may undergo this change. By examining different media with the spectrum in the manner already described, it is seen that the fluorescence begins, sometimes in the blue, sometimes in the yellow. With an alcoholic solution of chlorophyll, it begins in the red. But wherever the change of refrangibility may begin, it is always in one direction, consisting in a diminution of the index of refraction, and a consequent depression of the light in the scale of colours. In other words, the *length of the wave is increased, and its velocity of undulation diminished.* The vibrations of the ether in the incident ray appear to excite disturbances within the complex molecules of the fluorescent medium, whereby new vibrations are excited in the ether, differing in period from those of the incident ray. The portion of the light which has produced this molecular disturbance is used up or *absorbed*, and thereby lost to visual perception, just as heat is converted into mechanical work. It is probable that the absorption of light always takes place in this manner. The well-known fact of the conversion of luminous rays into invisible calorific rays, is, as already observed, a striking instance of diminution of refrangibility accompanied by absorption.

As the most refrangible rays are the most active in producing fluorescence, it is natural that this effect should be most strikingly exhibited by the light of flames which are rich in those rays,—the flame of alcohol and of sulphur, for example. These flames do, in fact, produce the effect in a higher degree even than sunlight. An extremely beautiful effect is produced by exposing a number of highly fluorescent media, such as sulphate of quinine, infusion of horse-chesnut bark, and canary-glass, to the flame of sulphur burning in oxygen in a dark room.

The colour and composition of fluorescent light sometimes afford valuable aid in distinguishing between one substance and another, and in testing the purity of solutions. With a solution of a *pure substance*, the tint of the fluorescent light is almost perfectly constant. But this tint, it must be remembered, is that of the light *as emitted*, not as *subsequently modified* by absorption on the part of the solution, in case the solution be sensibly coloured, and some precautions are required in order to observe it correctly. The fluorescence observed in solutions from the barks of the horse-chesnut, ash, &c., was formerly attributed indiscriminately to the presence of æsculin, whereas a purified solution from the bark of the horse-chesnut exhibits a fluorescence very sensibly different from that of æsculin, which observation alone would suffice to show that the bark must contain some other fluorescent substance besides æsculin.

The best mode of observing the true fluorescent tint is to dilute the liquid considerably, and to pass into it a beam of sunlight, condensed by a lens fixed in a board in such a manner that as small a thickness of the liquid as possible shall intervene between the fluorescent substance and the eye. If a stratum of this thickness of the dilute solution is sensibly colourless, the tint of the fluorescent light will not be sensibly modified by subsequent absorption. But as direct sunlight is not always to be had, the following method, requiring only diffused daylight, may also be used, the solutions being pretty strong, or at least not extremely dilute.

A glass containing water and blackened internally at the bottom is placed at a window, and the solution to be examined as to its fluorescent tint is placed in a test-tube which is held vertically in the water, the top slightly inclining from the window, and the observer regarding the fluorescent light from above, looking outside the test-tube. Since by far the greater part of the fluorescent light comes from a very thin stratum of liquid next the surface by which the light enters, the fluorescent rays have mostly to traverse only a very small thickness of the coloured liquid before reaching the eye; the water permits the escape of those fluorescent rays which would otherwise be internally reflected at the external surface of the test-tube, and the intensity of the light of which the tint is to be observed is increased by foreshortening. (Stokes, Chem. Soc. J. xi. 19.)

The nature of the solvent must also be attended to. The colour of the fluorescent light is liable to change, not merely in passing from an alkaline to a neutral or acid solution, but even occasionally in passing from one neutral solvent to another.

The composition of fluorescent light, as revealed by the prism, occasionally presents peculiarities, but in such cases they are found to be connected with peculiarities in the mode of absorption, so that the two are not to be regarded as *independent* characters of a substance; and as the peculiarities in the absorption are, as a general rule, the more easily observed, it is only rarely that the analysis of the fluorescent light is of much use.

The distribution of fluorescence in the spectrum often affords valuable information, but its observation requires the use of somewhat complicated apparatus. The observation is restricted to times when the sun is shining pretty steadily (unless the observer has recourse to electric light, or at least lime-light); it is requisite to reflect the sun's light horizontally, without which the observation would be most troublesome; and unless the reflexion be made by the mirror of a heliostat, the continual change in the direction of the reflected light is most inconvenient. It is requisite to use at least one good prism, better two or three, which must be of tolerable size, in order to have light of sufficient intensity, and the prisms must be combined with a lens, which need not however be achromatic.

It has already been stated, as the result of experience, that the colour of the fluorescent light of a single substance is constant throughout the spectrum, or very nearly so. If, therefore, on examining a solution in a pure spectrum thus formed by projection, we find the fluorescence taking a fresh start *with a different colour*, we may be almost certain that we have to do with a mixture of two different fluorescent substances, the presence of which is thus revealed without any chemical process. If, however, the fluorescence of two fluorescent substances, which may be mixed together, begins at nearly the same point in the spectrum (as commonly happens when there is merely a slight difference of tint in the colour of the fluorescent light of the two susbtances), the coexistence of the two may escape detection when the mixed solution is merely examined in a pure spectrum; and in such cases a combination of processes of fractional separation with the observation of the tint of the fluorescent light is more searching. This is the case, for instance, with the mixture of æsculin and fraxin contained in a solution from the bark of the horse-chesnut.

As the occurrence of a decided difference of colour in the fluorescent light seen at two different parts of the spectrum implies, almost to a certainty, the presence of two different fluorescent substances, so, conversely, the exhibition of the same colour is an argument in favour of the identity of the substance producing the fluorescence at the two parts. We cannot, indeed, say that there may not be two substances present, the fluorescence of which commences at nearly the same part of the spectrum; but two different substances, the fluorescence of which commenced at two widely different parts of the spectrum, would certainly reveal themselves by the difference of colour. For experience shows that the refrangibility of the light emitted at any part of the incident spectrum, by the solution of a pure substance, extends nearly up to that of the point of the incident spectrum at which the fluorescence commences, but not much beyond; and though, in passing from one pure substance to another, variations do occur in the relative brightness of the rays of less refrangibility which compose the fluorescent light, yet, on the whole, there is so close a connection between the colour of the fluorescent light and the refrangibility of the rays by which the fluorescence is first produced, that a great variation in the one is incompatible with constancy or a mere trifling variation in the other. (Stokes, Chem. Soc. J. xvii. 312.)

Absorption.

All bodies are transparent to a certain extent; even metals, which are the most opaque of all substances, allow a small quantity of light to pass through them, when they are reduced to extremely thin leaves; thus gold-leaf laid upon glass transmits light of a green colour. On the other hand, there is no such thing as a perfectly transparent medium; even the air stops a certain quantity of light, when the thickness traversed by the rays is very considerable; on the tops of high mountains the stars appear much brighter than when seen from near the sea-level. For all ordinary thicknesses, however, colourless gases may be regarded as perfectly transparent.

Transparent media are colourless or coloured, according as they transmit the several rays composing white light, in the same or in different proportions. Thus a red glass is one which transmits the red rays more easily than those of any other colour. On viewing a solar spectrum through a piece of glass 1 millimetre thick, coloured with red oxide of copper, all the colours excepting the red disappear, the glass being opaque to all the more refrangible rays. Other media transmit rays of one or more colours, and stop the rest, and consequently exhibit compound colours by transmitted light: thus an ammoniacal solution of copper, when of a certain strength and thickness, stops all the rays excepting the red and the violet.

If rays which have passed through a red glass be passed through another glass of the same colour, the latter will absorb but a small proportion of the rays which fall upon it, because those which are incapable of passing through red glass have already been eliminated by the first medium; but if the second glass is green, it will stop the red rays, and the two together will form a perfectly opaque screen.

There is no medium which is absolutely colourless, that is to say, capable of transmitting rays of all colours in exactly the same proportion; even air, when seen through great thicknesses, appears blue; the colour of the sky is merely that of the atmosphere seen through a thickness of several miles; in like manner distant mountains appear blue, just as if they were seen through a blue glass.

On the other hand, to enable a medium to absorb the rays of one or more colours completely, it must have a certain thickness. Even metals, as already observed, when reduced to extremely thin films, transmit certain colours, and a plate of glass which, when of a certain thickness, stops all but the red rays of the spectrum, transmits a greater and greater number of coloured rays as its thickness is diminished, and at last appears almost colourless.

It was formerly supposed that the quantity of light absorbed was proportional to the thickness of the medium through which it passed, but later researches have shown that the law is more complicated. Suppose the medium divided into infinitely thin layers perpendicular to the direction of the rays which traverse it; and let a be the fraction, supposed constant, which represents the proportion between the quantity of light arriving at any layer, and that of the light which passes through unabsorbed. The quantity of light (supposed homogeneous) which arrives at the first layer being I, that which reaches the second will be Ia; that which arrives at the third will be Ia^2, and so on. If therefore e represents the thickness of the medium (equivalent to n layers), the intensity of the ray after having passed through this thickness, is given by the formula $i = Ia^e$. The intensity of the emergent light decreases therefore in geometric proportion, while the thickness of the medium increases in arithmetical proportion. The quantities absorbed by the successive layers follow a similar law, being, for the first layer $I - Ia = I(1-a)$; for the second, $Ia(1-a)$; for the third, $Ia^2(1-a)$, and for the n'th, $Ia^{n-1}(1-a)$.

Now let R, O, Y, &c., represent the intensities of the several principal colours composing a ray of incident light, the total intensity of the beam being therefore $R + O + Y + G + B + I + V$; also let r, o, y, &c., be the fractions of the several coloured rays which traverse, without absorption, a unit of thickness of the medium; then the intensity of a beam emerging from a layer whose thickness is e, will be

$$Rr^e + Oo^e Y + y^e + Gg^e + Bb^e + Ii^e + Vv^e.$$

The terms of this expression containing the smallest of the fractions r, o, y, &c., decrease most rapidly as e increases; the colours corresponding to the other terms will therefore predominate more and more, and the emergent tint will not be white, but will exhibit a compound tint depending on the relative magnitude of the several terms, Rr^e, Oo^e, &c. If the rays of any one colour, red for example, are less absorbed than the rest, it is always possible, by increasing the thickness of the film, to a certain extent, to obtain red rays sensibly homogeneous; for by increasing e, the ratios $Rr^e : Oo^e$, $Rr^e : Yy^e$, &c., may be increased in any required proportion. When, on the contrary, the quantities r, o, y, &c., differ but little from unity, and the thickness of the medium is small, the sum $Rr^e + Oo^e +$ &c., differs but little from that which represents the intensity of the incident ray; that is to say, the light is not perceptibly coloured.

The relative quantities of the several coloured rays absorbed by a coloured medium of given thickness, may be observed by viewing a line of light through a prism and the coloured medium. The spectrum will then be seen to be diminished in brightness in some parts, and perhaps cut off altogether in others. This mode of observation is often of great use in chemical analysis, as many coloured substances when thus examined afford very characteristic spectra, the peculiarities of which may often be distinguished, even though the solution of the substance under examination contains a sufficient amount of coloured impurities to change its colour very considerably. The following method of making the observation is given by Professor Stokes (Chem. Soc. J. xvii. 306):

A small prism is to be chosen of dense flint glass, ground to an angle of 60°, and just large enough to cover the eye comfortably. The top and bottom should be flat, for convenience of holding the prism between the thumb and fore-finger, and laying it down on a table, so as not to scratch or soil the faces. A fine line of light is obtained by making a vertical slit in a board 6 inches square, or a little longer in a horizontal direction, and adapting to the aperture two pieces of thin metal. One of the metal pieces is movable, to allow of altering the breadth of the slit. About the fiftieth of an inch is a suitable breadth for ordinary purposes. The board and metal pieces should be well blackened.

On holding the board at arm's length against the sky or a luminous flame, the slit being, we will suppose, in a vertical direction, and viewing the line of light thus formed through the prism held close to the eye, with its edge vertical, a pure spectrum is obtained at a proper azimuth of the prism. Turning the prism round its axis alters the focus, and the proper focus is got by trial. The whole of the spectrum is not, indeed, in perfect focus at once, so that, in scrutinising one part after another, it is requisite to turn the prism a little. When daylight is used, the spectrum is known to be pure by its showing the principal fixed lines; in other cases the focus is got by the condition of seeing distinctly the other objects, whatever they may be, which are presented in the spectrum. To observe the absorption-spectrum of a liquid, an elastic band is put round the board near the top, and a test-tube containing the liquid is slipped under the band, which holds it in its place behind the slit. The spectrum is then observed just as before, the test-tube being turned from the eye.

Fig. 668.

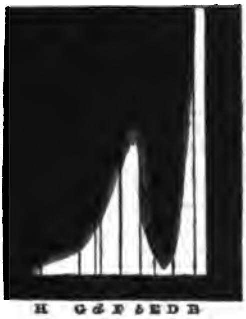
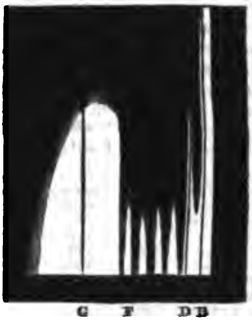


Fig. 669.



To observe the whole progress of the absorption, different degrees of strength must be used in succession, beginning with a strength which does not render any part of the spectrum absolutely black, unless it be one or more very narrow bands, as otherwise the most distinctive features of the absorption might be missed. If the solution be contained in a wedge-shaped vessel instead of a test-tube, the progress of the absorption may be watched in a continuous manner by sliding the vessel before the eye. Some observers prefer using a wedge-shaped vessel in combination with the slit, the slit being perpendicular to the edge of the wedge. In this case each element of the slit forms an elementary spectrum corresponding to a thickness of the solution which increases in a continuous manner from the edge of the wedge, where it vanishes. This is the mode of observation adopted by Gladstone. (Chem. Soc. J. lx. 79.)

Fig. 668 represents the effect produced in this way by a solution of sesquichloride of chromium, and *fig.* 669 that produced by a solution of permanganate of potassium. The right hand sides of these figures correspond with the red end of the spectrum; the letters refer to Frauenhofer's lines. The lower part of each figure shows the pure spectrum seen through the thinnest part of the wedge, and the progress of the absorption, as the thickness of the liquid increases, is seen by the gradual obliteration of the spectrum towards the upper part of the figures.

The following observations on the application of the absorption-method to chemical analysis, are extracted from a paper by Professor Stokes (Chem. Soc. J. xvii. 308):

"In many cases nothing is observed, beyond a general absorption of one or other end of the spectrum, or of its middle part, and the prism gives little information beyond what is obtained by the eye, by observing the *succession of colours* produced by different thicknesses of the liquid. And here it may be remarked in passing, with reference to the description of pure substances, that in specifying only one colour, that corresponding to a considerable thickness, as is commonly done by chemists, the peculiar features of the absorption are left almost wholly undescribed. Thus of two solutions, one might be pink when dilute, passing on to red with increase of strength and thickness, another yellow, passing through orange to red. These would commonly be described as red, yet the series of tints indicates an utter difference in the mode of absorption, the middle of the spectrum in the one case, and the most refrangible end in the other, being the most powerfully attacked.

"But in some cases, especially with substances of intense colorific power, the mode of absorption is eminently characteristic. Two or more dark bands are seen in the spectrum, indicating maxima of absorption; and the positions of these bands, their relative intensity, and their other features, form altogether a series of characters the distinctive nature of which is such as those who have neglected the use of the prism have little conception of. They render it perfectly easy in many cases to follow a particular substance among a host of impurities. For each coloured substance produces its own absorption, independently of the others (supposing the substances do not chemically react on each other), so that, unless the part of the spectrum in which the distinctive bands, or most of them, occur, is wholly absorbed by the impurities, the presence of the substance can still be recognised. Such a complete obliteration is the less likely to occur, for this reason, that when the characters of the solution are so strongly marked, it almost always happens that a comparatively small quantity of the substance suffices to produce the effect, and the solution must consequently be so much diluted that the effect of the impurities comparatively disappears.

"Nor is this all. When a substance exhibits marked characters of one kind in one solvent, it often happens that it shows different and no less marked characters in a solvent of a different nature. Not only does this furnish additional characters by which the substance can be distinguished from others, but it is valuable for following the substance when involved in impurities: for the nature of the impurities may be such as to mask the substance in one solvent and not in another. This is especially the case where one solvent is alkaline and the other acid; but differences are sometimes observed even with two neutral solvents.

"To illustrate these principles, we may refer to the colouring matters of madder Alizarin and purpurin both yield highly distinctive spectra, the former, however, only in the case of solutions containing caustic alkali,[*] whereas most solutions of the latter are highly distinctive. Madder itself contains, either directly or as the result of decomposition, a number of substances which, in alkaline solution, absorb that part of the spectrum in which the distinctive bands of purpurin occur. Hence, in a mixture obtained from madder, and containing, we will suppose, purpurin in comparatively small quantity, the presence of purpurin would, *in an alkaline solution*, be masked by the other substances. But in ether or acidulated alcohol the other substances yield spectra showing nothing particular, and interfering comparatively little with the distinctive bands of purpurin; while in an alum-liquor solution made by boiling, not only are the purpurin bands, which in this solvent occur at a lower refrangibility than with ether, more effectually separated from the absorption produced by the associated substances, but those substances themselves are also in good measure excluded.

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[*] A solution of alizarin in carbonate of potassium or sodium, or in ammonia, exhibits a spectrum having a band of absorption in the yellow, another narrower one between the red and the orange, and a third very inconspicuous band coinciding with the line E.—Purpurin, dissolved in carbonate of potassium or sodium, exhibits two dark bands of absorption about the green part of the spectrum.—A solution of the same substance in aqueous alum exhibits the same peculiar mode of absorption, but likewise a yellow fluorescence.—A solution of purpurin in sulphide of carbon exhibits four bands of absorption, of which the first, situated in the yellow just beyond D, reckoning from the red extremity, is narrower than the rest; the second is situated in the green, nearly coinciding with the line E; the third in the blue near F; and the fourth, which is very inconspicuous, in the indigo.—Lastly, the solution of purpurin in ether gives a spectrum exhibiting two bands of absorption; one narrow and very dark in the green, nearly coinciding with E; the second in the blue, broader and less strongly marked, and having its centre at the line F; the solution is also slightly fluorescent. (Stokes, Chem. Soc. J. xii. 220.)

"For an example of the necessity of attending to the nature of the solvent, even in the case of different neutral solvents, we may refer to a yellow substance which is one of the constituents of the green colouring matter of leaves. The alcoholic solution of this substance exhibits two characteristic bands of absorption, the first of which is situated immediately adjacent to the line F on the more refrangible side. The solution in sulphide of carbon exhibits two similar bands, but much less refrangible, the line F now nearly bisecting the bright interval betweeen the first and second dark bands. The substance is very easily decomposed by acids, and even by acid salts, yielding a product of decomposition which, in alcoholic solution, exhibits two bands of absorption, like the parent substance, but a good deal more refrangible. There is the same change of position as in the former case, in passing from alcohol to sulphide of carbon, so that the solution of the product of decomposition in sulphide of carbon agrees almost exactly, in colour and spectrum, with that of the parent substance in alcohol.

"Not only is an examination of the absorption-spectrum of a substance useful for enabling us to follow the substance through mixed solutions, but it sometimes reveals relationships in cases in which they might not be suspected, if the origin of the substances were unknown. Thus, the purpureïn of Dr. Stenhouse dissolves in ether or acidulated alcohol with a red colour, while that of the same solutions of purpurin is yellow. But the prism reveals, in both cases alike, the existence of three bands of absorption, of similar breadth, while the purpureïn bands are situated nearer the red than those of purpurin, by about one interval. This example shows how deeply seated in the molecular constitution of a body may in some cases be the cause which produces the bands.

"Hitherto it has been supposed that the peculiarities of absorption of a substance were known and applied to the detection of that substance in a mixture. But the question may arise:—Given a mixture of an unknown number of unknown substances, which as a whole presents peculiarities of absorption, to determine whether the whole of these peculiarities are due to the same substance, and, if not, what portion are due to one substance, and what portion to another. Little can be done towards the solution of this problem by the mere observation of absorption; we can only say, that some modes of grouping of bands of absorption are common in solutions of pure substances, while others are uncommon, and give rise to the suspicion of a mixture. The phenomena of fluorescence give in some cases material assistance; but in general it is only by combining spectral analysis with processes of chemical separation, especially fractional separation, that a satisfactory conclusion can be arrived at. When a mixture is thus tested in various ways, a conviction, at last approaching certainty, is gradually arrived at, that those bands of absorption which are always found accompanying one another belong to one and the same substance.

"For convenience and rapidity of manipulation, especially in the examination of very minute quantities, there is no method of separation equal to that of partition between solvents which separate after agitation. Ether combined with water, either pure or rendered acid or alkaline, is the most generally useful, and the separation, if not otherwise fractional, may be rendered so by introducing the acid or alkali by minute quantities at a time; but other solvents are useful in particular cases. Sulphide of carbon in conjunction with alcohol affords the means of disentangling the coloured substances which are mixed together in the green colouring matter of leaves. Solutions of various metallic oxides which are naturally precipitable by an alkali or alkaline carbonate, but are retained in solution by means of a tartrate, are very useful in the examination of the true colouring matters, not merely for producing changes of colour and spectrum without precipitation, but even, in conjunction with ether, for effecting chemical separation: and fractional separation may be effected by making the solution deviate very slightly from perfect neutrality. By combining with ether such a solution of alumina, it was found possible to separate and detect the purpurin, alizarin, and rubiacin present in a portion of powder not exceeding in bulk a fraction of the head of a pin." (Stokes.)

The following observations on the absorption spectra of metallic salts are by Dr. Gladstone (Chem. Soc. J. x. 79):

A comparison of the spectra exhibited by different salts, only one constituent of which is coloured, shows that, with very few exceptions, all the compounds of the same base or acid have the same effect on the rays of light. This law is seen to hold good in many instances which at first sight appear exceptional. Thus it is well known that some salts of chromic oxide are green, others red or purple. Now these differently coloured chromic salts all exhibit the same general form of spectrum (*fig.* 668), in which the violet and indigo rays are very soon cut off; and as the thickness increases, the light is more and more concentrated about two points—one in the red, the other in the bluish-green, the red ray penetrating with the greatest facility. Hence it is that the chloride and other salts of chromium, which are green in moderately dilute solutions, appear purple or red when we look through a strong or very deep solution. The acetate absorbs the green rays more readily, and therefore appears green only in very weak solutions, or in thin strata, while the "red potassio-oxalate" absorbs the green so speedily that the thinnest portion of it appears bluish-red.

Salts composed of a coloured base and a coloured acid exhibit colours compounded of the rays which are not absorbed by either, the resultant colour bearing, in many instances, but little resemblance to the original colours. Thus, the acid chromate of chromic oxide, a compound of two substances which give respectively yellow and green solutions, is not bright green, but brownish-red, because the chromic acid cuts off nearly all the blue and violet rays, while the oxide of chromium absorbs the yellow and the greater part of the green.

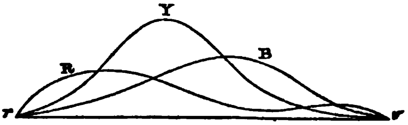
Some salts which are but slightly coloured, nevertheless exhibit very characteristic spectra. Thus, a solution of sulphate of didymium, which has but a faint rose colour, exhibits, when examined by the hollow wedge and prism, a spectrum containing two very black lines; one in the yellow, the other in the green. These lines are visible in very weak solutions of didymium, and therefore serve as a delicate test for that metal; they, moreover, afford means of distinguishing it from cerium and lanthanum, in the spectra of which they do not occur.

Brewster's Theory of the Spectrum. Newton regarded the spectrum as composed of an infinite number of simple colours, each element of it consisting of a ray of definite refrangibility and not capable of further decomposition; and this theory has been almost universally received as affording satisfactory explanations of all the phenomena of colour, and of the decomposition and recomposition of light. Brewster, however, in studying the decomposition of light by absorption, observed certain facts which he regarded as incompatible with Newton's theory, and he accordingly proposed a new theory of the constitution of the spectrum, which is as follows:—

1. White light is composed of *three* colours only, red, yellow, and blue, mixed in certain proportions.

2. The solar spectrum is formed of three superposed spectra of these colours, each of them extending the entire length of the spectrum, but with varying intensities as shown in *fig.* 670; where the horizontal line *rv*, represents the length of the spectrum, and the three curves, R, Y, and B, are so drawn that their ordinates are proportional to the intensities of the several colours at each point, the blue having a maximum between the fixed lines F and G, the yellow near F, and the red, two maxima, one near B, and another of lower intensity near the violet end of the spectrum.

Fig. 670.



3. All the colours of the spectrum are compound, and as all the rays united in one point have the same degree of refrangibility, they cannot be further decomposed by refraction.

Brewster was led to these conclusions by observing that when the spectrum is viewed through certain coloured media, white light may be shown to exist in any part of it. Thus, by looking through an azure-blue glass of sufficient thickness, or better, through a solution of sulphate of copper mixed with red ink, the yellow of the spectrum is replaced by white, very slightly tinged with green or red, according to the particular tint of the medium. This white light is not decomposible by refraction, but may be decomposed by viewing it through a film of gelatin of yellow or green colour, the white band then appearing yellow or green, in consequence of the absorption of the blue or red rays. By similar means Brewster found white light in the green and the orange, whence he concluded that the three primary colours exist in the yellow, green, and orange of the spectrum. In like manner, by viewing the spectrum through certain yellow liquids, he found that the blue and indigo assumed a violet tint, whence he concluded that red light exists in these parts of the spectrum. The blue of the spectrum seen through a film of blue gelatin, exhibited a white band, and the blue and indigo viewed through a blue glass assumed a violet tint: hence the presence of yellow in the blue was inferred. By viewing the spectrum through a layer of Peruvian balsam, pitch, sulphur-balsam or red mica, yellow was seen in the red near the line C. Brewster was not able to detect yellow in the violet, but he attributed this negative result to the feebleness of the light in this part of the spectrum, and the facility with which it is absorbed by all coloured media. Lastly, the red of the spectrum seen through balsam of Peru, pitch, sulphur-balsam, or red mica, appeared green, whence it was inferred that the red of the spectrum also contained blue.

Brewster's theory has not however met with general adoption. In the first place, it is quite inconsistent with the wave-theory of light: for just as there is an infinite number of sounds corresponding with an infinity of wave-lengths in the air, so likewise must there be an infinite number of shades of colour corresponding with an infinite number of wave-lengths in the ether, and therefore also (p. 609), an infinite number of different refrangibilities. On the other hand, to account for the dark lines of the solar spectrum, it would be necessary to suppose that certain rays are wanting in the component spectra exactly at the same points, which is very improbable.

Moreover there is no reason whatever for assuming that red, yellow, and blue are the component colours of white light; indeed, Helmholtz has shown, by a method to be presently described, that the actual colours of the spectrum may be more exactly imitated by combinations of red, green, and violet, but that even then the imitation is far from satisfactory.

More careful observations by Airy, Helmholtz, and others have likewise shown that Brewster's conclusions are not borne out, even by his own method of observation, when proper precautions are taken to eliminate sources of error. Airy has pointed out that to obtain correct results with such a mode of experimenting, it is necessary in the first place to exclude all extraneous light, which, being decomposed by the coloured medium, will modify the tint observed; and, secondly, to compare the spectrum viewed through the coloured medium with a pure spectrum viewed directly, the two being formed immediately one above the other, as in no other way can an exact comparison of the tints in the corresponding parts of the two be made. When these precautions were taken, he found it impossible to distinguish the slightest difference, excepting in brightness, between the colours of the spectrum seen through a coloured medium, and those of the spectrum viewed directly. Airy also observes that the intensity of the light may make a great difference in the impression produced on the eye by any particular colour.

Helmholtz has shown that the results may be modified by the light scattered by irregular refraction at the surfaces of the coloured medium, and by the lens and prism used to form the spectrum, especially when the absorbent medium used is a film of gelatin, which is not very transparent. To eliminate this diffused light, the spectrum is received on a screen having a narrow slit through which a thin coloured pencil can pass, and this pencil is made to fall upon a second prism, followed by a lens, which forms a coloured image of the slit, and a faint spectrum proceeding from the diffused light which has passed through the second aperture. This spectrum does not perceptibly alter the purity of the focal image. On examining the different colours of this purified spectrum through various coloured media, it was found impossible to distinguish any difference of tint between the colours thus observed and those viewed directly.

From all these experiments it may be inferred that it is impossible to decompose the colours of the spectrum by absorption any more than by refraction; that the colours, as Newton supposed, are simple; and that to each colour there corresponds a definite degree of refrangibility.

Decomposition of Light by Reflection.

Newton explained the colours of bodies by supposing that they decompose the light which falls on their surfaces, absorbing some of the component rays, reflecting the rest in a diffused manner if they are opaque, or reflecting one portion and transmitting another if they are transparent, the reflected and transmitted light being always more or less coloured, because the different coloured rays are not absorbed in the same proportion. Black substances are those which absorb all the rays which fall upon them; white substances, those which reflect all the rays; bodies of these two classes act in the same manner on all kinds of luminous rays. But between these two extremes, there is an infinity of substances which reflect the several coloured rays in different proportions. A red body, for example, is one which reflects red in larger proportion than the other rays composing white light. In the case of opaque bodies the decomposition of the light takes place at an insensible depth below the surface, the result being independent of the inner layers of the substance.

If rays of light dispersed by a prism be thrown on a *white* surface, each point reflects the light which it receives, and appears of the same colour as that light. If the surface is *red*, it appears very bright in the red part of the spectrum, but the other colours are faint, the red surface reflecting the red rays of the spectrum abundantly, but the other colours in small proportions only. If the body is capable of absorbing certain rays completely, black bands are seen in the corresponding parts of the spectrum, and if the body be illuminated solely by rays of that particular degree of refrangibility, it appears black.

A coloured body illuminated by different sources of light may exhibit different colours, the spectra formed by the light from these several sources not being formed of the same colours or in the same proportions. It is thus that objects which are green by daylight appear blue by lamp-light, the yellow rays being less abundant in the light of ordinary flames than in solar light. Most objects appear differently coloured by moonlight, from what they do by daylight. When a series of the seven principal colours of the spectrum is illuminated by the monochromatic yellow light of a lamp fed with spirit containing common salt, the yellow, orange and red strips appear yellow of various degrees of brightness, the rest grey or black, because they do not receive rays which they are capable of reflecting, or in other words, because their particles are not susceptible of vibrating in unison with those of the light which falls upon them. In the same light, the face and lips appear of a livid hue, because the red rays which the skin reflects in daylight are wanting in the yellow light.

When the body on which the light falls is transparent, the rays which pass through it are those which have not been reflected at its surface; hence the reflected and transmitted light may be of different colours. Such is in fact the case in many instances. Gold-leaf, which is yellow by reflected light, transmits light of a bluish-green colour. Faraday formed pulverulent deposits by sending powerful electric discharges through metallic wires in an atmosphere of hydrogen; in the finely-divided state thus produced, copper appeared green by transmitted light; tin, brown; zinc, brown or bluish-grey; palladium, brown; aluminium, brown or orange-coloured. The reflected and transmitted rays are sometimes complementary to each other; but this is the case only when no part of the light is absorbed. When a body exhibits the same colour, red for example, both by reflection and by transmission, it is because it reflects part of the red rays of the incident light, transmits the rest, and absorbs the rays of all the other colours.

In many cases, however, as pointed out by Professor Stokes (Chem. Soc. J. xvii. 315), the colour of a body attributed on cursory examination to reflection, is really due to transmission; in fact, the instances in which substances appear coloured by reflection are comparatively rare. "A chemist views a solution contained in a test-tube by transmission and then by reflection; and seeing perhaps some perfectly different colour in the latter case, describes it as the colour of the solution by reflection, whereas it is merely the colour by transmission due to a greater thickness, the light having been reflected at the back or bottom of the test-tube, and so having twice passed through the solution. In other cases, the colour described as due to reflection really arises from fluorescence; and though the statement may be true in the sense intended, it seems objectionable to apply the term *reflection* to a process so utterly different. It is only in the case of metals, such as gold and copper, and of certain other substances, such as murexide, platinocyanide of magnesium, &c., that colour is really seen as the result of reflection.

"When this takes place in the case of non-metallic substances, they are found to be endowed, for the colours so reflected, with an intense opacity, comparable with that of metals; while for other parts of the spectrum, they may be comparatively transparent, and these parts they reflect with an energy comparable to that of a vitreous substance only. The variations of absorbing power in passing from one part of the spectrum to another, and consequently the variations in reflecting energy, are frequently much more considerable, and accordingly the colour by reflection is much richer than in the case of metals."

"An excellent example of the intimate connection between metallic reflection and intense absorption is afforded by the crystals of permanganate of potassium. These crystals exhibit a green metallic reflection, and when crushed yield a powder of an intense purple colour by transmitted light. The colour is too intense for spectral analysis, but the solution has a similar colour, merely less intense as corresponds with its smaller concentration, and the analysis of the light transmitted by the solution presents no difficulty. The green is quickly absorbed, but when the solution is sufficiently dilute, five eminently characteristic bands of absorption are seen in that part of the spectrum. A sixth band comes out with a greater thickness or else strength of solution, but even the fifth is somewhat less strong than the others. When the light reflected from a crystal is analysed, four bright bands are seen standing out on a generally luminous ground of inferior brightness. These bright bands correspond in position with the principal *dark* bands in the light transmitted by the solution, and therefore, it may be presumed, by the crystals themselves. When the angle of incidence has a suitable value, and the reflected light is analysed by a Nichol's prism, with its principal plane in the plane of incidence, and then by a common prism, the spectrum is reduced to these four bright bands. A fifth bright band could, perhaps, be made out, in the case of a fine crystal with a fresh surface. Under the circumstances described, the Nichol's prism would extinguish the light reflected from a vitreous substance, and transmit much of that reflected from a metal. We see, therefore, that, as regards its relations to light, the crystallised body passes repeatedly from the condition of a vitreous to that of a metallic substance and back again, as the refrangibility of the rays, in relation to which it is considered, is continuously increased by a small amount.

"The same relation between intense absorption and metallic reflection exists generally, though it cannot be always studied by means of a solution. The platinocyanides, for example, yield colourless solutions, so that the intense absorption which most of them exercise for certain parts of the spectrum must be attributed to the mode in which the molecules are built up in forming the crystals; but by attending to the colour of the light transmitted by thin crystals, the law is found to be obeyed. Gold can only be obtained, in solution, as gold by means of the opaque solvent mercury; but its colour by transmission may be studied in gold-leaf, or in a chemically deposited film, and is then found to be conformable to the law mentioned, the less refrangible colours, which are those which are the more copiously reflected, being also those which are the more intensely absorbed.

"When a body endowed with the property of coloured reflection, such as permanganate of potassium, is dissolved, in consequence of the necessary dilution, the opacity of the medium ceases to be, for any part of the spectrum, of that intense kind which is necessary for quasi-metallic reflection; and accordingly the light reflected by the solution is colourless.

"In order that the colour due to reflection should appear, it is necessary that the substance should have a certain amount of coherence. Thus indigo in the form of a fine loose powder is blue, even when viewed by reflection. It would be erroneous, however, to describe the body as blue by reflection, if we were speaking of the properties of the substance, and not the mere crude results of observation made under given circumstances. For though it is true that the light by which the blue colour is seen has undergone reflection (without which it would not have reached the eye) it is not *in reflection* that the chromatic selection is made by virtue of which the powder appears blue, but *during transmission*. In fact it is only a small portion of the light that is reflected at the outer irregular surface of the mass; the greater part penetrates a little way, and is reflected at various depths, and in passing through the particles, in going and returning, suffers absorption on the part of the coloured substance. Were the substance intensely opaque for *all* the colours of the spectrum, the powder would be not blue but black, as we see in the case of platinum-black. By burnishing, the powder is reduced to the state of a somewhat coherent mass, and it now begins to exhibit the copper colour due to reflection. The internal reflections are at the same time greatly weakened, so that the part of the light which is reflected from beneath and undergoes absorption is much reduced. A pressed mass is not, however, an optically homogeneous medium, so that the colour by reflection obtained by burnishing cannot in general be quite pure. In the state of a fine crystalline powder, indigo exhibits a mixture of the copper colour due to reflection, and the blue colour due to transmission, though observed in the light reflected from the mass as a whole; while if the substance could be obtained in large crystals, the colour by reflection would be seen in perfection, and the colour by transmission would disappear, the crystals being sensibly opaque." (Stokes.)

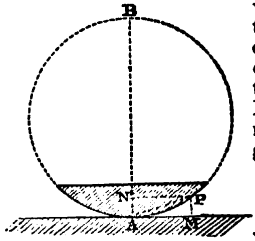
The Colours of Thin Plates.

All transparent substances, when reduced to very thin films, exhibit brilliant colours —a soap-bubble affords a familiar instance of this; glass blown out into thin films exhibits similar phenomena—so, likewise, does a layer of oil spread over the surface of water. These effects, however, are best studied in the case of a thin film of air formed between two plates of glass. When two glass plates (of any sort of glass) are pressed hard together, a black spot is observed at the point of closest contact, and around it a series of fringes exhibiting remarkably beautiful colours: if the light be homogeneous, as that of a soda flame, the bands are alternately light and dark. The shape of the bands depends upon the greater or lesser regularity of thickness in the film of air. If the glasses be so pressed at one point that the intervening space shall increase regularly all round, the bands will be circular—otherwise they will have an irregular shape—but in all cases the same thickness of the film of air gives, *cæteris paribus*, the same colour. Newton, to whom this experiment is due, made use of a plano-convex lens of small curvature, resting on a piece of flat glass: by this means he obtained a film of air whose thickness was uniform at the same distance from the point of contact, and the fringes were consequently circular. By this arrangement also, knowing the diameter of the lens, he was enabled to calculate the thickness of the film of air by which any particular band was produced. For, the radius of the ring AM (*fig.* 671) being found by measurement, and the diameter of the lens AB being also given, we have $AB \times AN$ (or MP) $= AP^2 = AM^2$ (nearly);

$$\text{therefore } MP = \frac{AM^2}{AB},$$

whence also MP varies as AM^2.

Fig. 671.



Proceeding in this manner, Newton found that the thicknesses of the films of air by which the successive dark bands were formed varied in the ratio of the even numbers

$$0, 2, 4, 6, \quad . \quad . \quad . \quad . \quad 2n;$$

and those by which the light bands were produced in the numbers

$$1, 3, 5, 7, \quad . \quad . \quad . \quad . \quad 2n+1;$$

further, that the thickness of the film at the first bright band was 6-millionths of an inch for red light, and about $4\frac{1}{2}$-millionths for violet light.

Now comparing these numbers with those afterwards found by Fresnel for the lengths of the waves (p. 600), it is found that the thickness of the film in question $= \frac{1}{4}$ of the length of a wave.

The explanation of this phenomenon is as follows:—The bands are formed by the interference of rays reflected from the upper and under surfaces of the transparent film. Now at the centre, where the two surfaces are in almost absolute contact, we might expect the reflected rays to be in accordance—for they reach the eye after travelling over equal paths. At the first bright band, the thickness $= \frac{1}{4}$ of an undulation; hence the ray reflected from the second surface, which has to traverse this thickness twice, is behind the other by half an undulation, and might therefore be expected to destroy the other: but instead of that, the two assist each other and produce a bright band; similarly with the other bright bands, which are produced by rays whose paths differ in length by

$$\tfrac{3}{2}, \tfrac{5}{2}, \tfrac{7}{2}, \quad . \quad . \quad . \quad \frac{2n+1}{2} \text{ of a wave-length.}$$

The dark bands are formed by rays which differ by

$$0, \tfrac{2}{2}, \tfrac{4}{2}, \tfrac{6}{2}, \quad . \quad . \quad . \quad \frac{2n}{2} \text{ of a wave-length,}$$

and which might therefore be expected to be in accordance.

The explanation of this apparent anomaly is found, as pointed out by Young, in the manner in which the direction of the vibrations of the ether-molecules is changed in passing from one medium to another.

When a wave of light travels through a medium of uniform constitution, it never returns upon its path; no reflection takes place, but each particle, when thrown into a state of vibration, communicates its vibration to the next, and is itself brought to rest; just as an ivory ball striking upon another of equal size, drives that ball forward, but is itself brought to rest. But if the vibration is communicated to a medium of different constitution—as when a ray passes from air into glass, or from glass into air—this complete destruction of the vibration of the particles does not take place; and the consequence is, that the light is at the same time transmitted through the second medium, and reflected back into the first. If the ray passes from a medium in which the ether is of greater density to one in which it is of less density, as from glass into air, the direction of vibration of the particles in the reflected ray remains unchanged, just as a large billiard ball striking a small one, drives the small one before it, and continues in its own course though with less velocity. In the contrary case, as when the ray passes from air to glass, that is to say, from ether of less density to ether of greater density, the vibration of the particles in the reflected ray is *reversed*—just as when a small ball strikes a large one, the large ball is driven forward but the small one driven back upon its path.

To apply this to the case of Newton's rings. The bands are formed by the interference of rays reflected from the first surface with rays reflected from the second surface of the film of air. Now in the second reflection, according to the principle just explained, the vibration in the particles of the reflected ray is reversed, because the ray passes from air to glass, whereas at the first surface, where the ray passes from glass to air, no such reversal takes place. Consequently the two rays, when they meet, will have their vibrations in accordance, just when they would have been in discordance if the reversal of vibration at the second surface had not taken place. Hence the dark bands are produced where the thickness of the film is

$$0,\ 2d,\ 4d,\ 6d\ \ .\ \ .\ \ .\ \ 2nd,$$

and the bright bands where the thickness is

$$d,\ 3d,\ 5d,\ 7d\ \ .\ \ .\ \ .\ \ (2n+1)\,d$$

d being $= \frac{1}{4}$ of an undulation.

That this is the true explanation of the phenomenon is proved by the fact that when a film of a transparent substance is placed between two other media, one of greater and the other of less refracting power than itself, the positions of the light and dark bands are reversed. Thus when a film of oil of sassafras is placed between a plate of crown and a plate of flint glass, the central spot is *white;* and the thicknesses of the film follow the ratio of the odd numbers for the dark, and of the even numbers for the light bands.

To return to the ordinary case of a film of air between glass plates. Fringes are produced by *transmitted,* as well as by reflected light, but the colours of any particular ring are exactly complementary of those of the same ring formed by reflected light; and if the light be homogeneous, the central spot is light, and the bands follow the reverse order of that which they do when formed by reflected light. These transmission fringes are formed by the interference of rays transmitted through the film, with other rays which pass through it after having undergone two reflections, one at the second surface, and the other at the first; and since both these reflections are made in passing from air to glass, the change of direction caused by the first reflection is again reversed by the second, and consequently the rays are in accordance or discordance, just when they would have been in case of no reflection at all.

Relation between the Indices of Refraction and the Thicknesses of the Films.—The thicknesses of thin plates of different substances, at the points where they form coloured bands of the same order, are to one another *in the inverse ratio of their indices of refraction.*

Consider, for example, the bright fringe of the *m*th order. If λ, λ' are the wavelengths of the homogeneous light in the two substances, and e, e' their thicknesses, we have the equations,

$$e = (2m + 1)\tfrac{1}{2}\lambda;\ e' = (2m + 1)\tfrac{1}{2}\lambda';$$

therefore $e : e' = \lambda : \lambda' = \mu' : \mu$.

Newton discovered this law by experiment. It may be verified for air and water by introducing a drop of water between the two glass plates which produce the rings, the water then penetrating between the plates by capillarity, and expelling the air from part of the circular space around the point of contact. It will then be observed that the fourth ring in air coincides with the fifth ring in water. Now the thicknesses of the film at the several bright rings in air are, e, $3e$, $5e$, $7e$, $9e$, &c., and in water e', $3e'$, $5e'$, $7e'$, $9e'$, &c.; the result just described gives, therefore, $7e = 9e'$; whence $\frac{e}{e'} = \frac{\mu'}{\mu} = \frac{9}{7}$, which is the index of refraction of water referred to air as unity.

This law furnishes an additional method of measuring the indices of refraction of liquids with respect to air; for in the expression $e : e' = \mu' : \mu$, the ratio of the thicknesses may be replaced by that of the squares of the diameters of the rings of the same order, whence the refractive index of the liquid may be calculated as a function of that of air. The method is not however very exact, in consequence of the difficulty of measuring the diameters of the rings.

We have hitherto supposed that the eye is placed directly over the centre of the rings, so that they are seen by perpendicular incidence. If the eye be moved from this position, so as to view the rings obliquely, these diameters increase as the incident rays become more and more oblique; that is to say, the thickness of the transparent film corresponding to a ring of given order increases with the obliquity of the rays; in other respects, the diameters of the rings follow the same laws as when the incidence is perpendicular. Newton found by experiment, that the thickness e, of a ring of given order seen by perpendicular incidence, is connected with the thickness e, for the same ring viewed at the incidence i—supposing the thin film to be formed of the same substance as the medium which surrounds the apparatus—by the equation, $e = e' \cos i$, or $e' = e \sec i$.

The diameters of the rings, like the breadths of all other interference-fringes, are greatest in red, and least in violet light; hence in white light a series of coloured rings is produced not separated by any absolutely dark spaces.

The following table exhibits the succession of colours produced by thin films or plates, and the corresponding thicknesses of three different media:

Newton's *Table of the Colours of Thin Plates in Air, Water, and Glass.*

Succession of *Spectra* or *Orders* of Colours.	Colours produced at the thicknesses in the last three columns.		Thicknesses in millionths of an inch.		
	Reflected.	Transmitted.	Air.	Water.	Glass.
First Spectrum or Order of Colours	Very black		$\frac{1}{2}$	$\frac{3}{8}$	$\frac{10}{31}$
	Black	White	1	$\frac{3}{4}$	$\frac{20}{31}$
	Beginning of black		2	$1\frac{1}{2}$	$1\frac{2}{7}$
	Blue	Yellowish-red	$2\frac{2}{5}$	$1\frac{4}{5}$	$1\frac{11}{20}$
	White	Black	$5\frac{1}{4}$	$3\frac{7}{8}$	$3\frac{2}{5}$
	Yellow	Violet	$7\frac{1}{9}$	$5\frac{1}{3}$	$4\frac{3}{5}$
	Orange		8	6	$4\frac{1}{6}$
	Red	Blue	9	$6\frac{3}{4}$	$5\frac{4}{5}$
Second Spectrum or Order of Colours	Violet	White	$11\frac{1}{6}$	$3\frac{3}{8}$	$7\frac{1}{5}$
	Indigo		$12\frac{5}{6}$	$9\frac{5}{8}$	$8\frac{2}{11}$
	Blue	Yellow	14	$10\frac{1}{2}$	9
	Green	Red	$15\frac{1}{8}$	$11\frac{2}{3}$	$9\frac{5}{7}$
	Yellow	Violet	$16\frac{2}{7}$	$12\frac{1}{5}$	$10\frac{2}{5}$
	Orange		$17\frac{2}{9}$	13	$11\frac{1}{9}$
	Bright red	Blue	$18\frac{1}{3}$	$13\frac{3}{4}$	$11\frac{5}{6}$
	Scarlet		$19\frac{2}{3}$	$14\frac{3}{4}$	$12\frac{2}{3}$
Third Spectrum or Order of Colours	Purple	Green	21	$15\frac{3}{4}$	$13\frac{11}{20}$
	Indigo		$22\frac{1}{10}$	$17\frac{4}{7}$	$14\frac{1}{4}$
	Blue	Yellow	$23\frac{2}{5}$	$17\frac{11}{20}$	$15\frac{1}{10}$
	Green	Red	$25\frac{1}{5}$	$18\frac{6}{10}$	$16\frac{1}{4}$
	Yellow	Bluish-green	$27\frac{1}{7}$	$20\frac{1}{3}$	$17\frac{1}{2}$
	Red		29	$21\frac{3}{4}$	$18\frac{5}{7}$
	Bluish-red		32	24	$20\frac{2}{3}$
Fourth Spectrum or Order of Colours	Bluish-green		24	$25\frac{1}{2}$	22
	Green	Red	$35\frac{2}{7}$	$26\frac{1}{2}$	$22\frac{3}{4}$
	Yellowish-green		36	27	$23\frac{2}{9}$
	Red	Bluish-green	$40\frac{1}{3}$	$30\frac{1}{4}$	26
Fifth Spectrum or Order of Colours	Greenish-blue	Red	46	$34\frac{1}{2}$	$39\frac{2}{3}$
	Red		$52\frac{1}{2}$	$39\frac{3}{8}$	34
Sixth Spectrum or Order of Colours	Greenish-blue		$58\frac{3}{4}$	44	38
	Red		65	$48\frac{3}{4}$	42
Seventh Spectrum or Order of Colours	Greenish-blue		71	$53\frac{1}{4}$	$45\frac{4}{5}$
	Reddish-white		71	$57\frac{3}{4}$	$49\frac{2}{3}$

Beyond these limits, the colours become mixed to such an extent as to produce white light. If, however, the rings be viewed through a prism, so as to separate the different coloured rays, a much larger number of them will come into view.

The transmitted rings are much fainter than the reflected rings, because one of the beams of light which contribute to their formation has been twice reflected, and each reflection is attended with a considerable loss of light.

We have been particular in describing the colours of 'Newton's rings,' because they are generally used as a standard of comparison for all coloured phenomena depending upon interference.

Colours of Thick Plates.—This term is applied to certain systems of coloured rings or fringes, produced by interference at the surfaces of transparent media, too thick to exhibit the peculiar phenomena known as the colours of thin plates. Newton, having received on a concave mirror of silvered glass a thin beam of solar light passing into a dark room through a small aperture situated at the centre of curvature of the mirror, perceived round the aperture a series of coloured rings having the violet turned inwards, as in the colours of thin plates. With homogeneous light, the rings were alternately bright and dark. Newton found by measurement—1. That the diameters of the rings were regulated by the same laws as those of the rings formed by transmission in thin plates. 2. When different kinds of homogeneous light are employed, the ratios of the diameters are the same as in thin plates. 3. The diameters of the rings formed by mirrors of equal radius and different thickness, are inversely as the square roots of the thicknesses.

The formation of these rings depends, however, on a condition which Newton did not observe, viz., that the upper surface of the mirror must not be quite bright. If this surface is well polished and carefully cleansed, the rings are scarcely visible; whereas if the surface is made dull by breathing or throwing dust upon it, or by covering it with a thin coat of varnish, or of water whitened with a little milk, which is then allowed to dry, they come out with great brightness. If, on the other hand, the silvering be removed from the back of the mirror, the rings become very faint, and with a metallic mirror none at all are produced. These experiments show that the rings are produced by the interference of rays reflected from the second surface of the mirror, with diffused light reflected from the first surface, which has been dulled. This is rendered further evident by an experiment of the Duc de Chaulnes, who, instead of a glass mirror, used a metallic mirror, before which he placed a piece of plate glass having its surface somewhat tarnished, or a plate of mica, either of which fulfilled the same purpose as the anterior surface of the glass mirror.

Pouillet, instead of a transparent plate, places in front of the mirror a screen, pierced with an aperture *of any form whatever*, but small enough to cause both the incident rays and those reflected from the mirror to come in contact with its edges. A straight-edged screen, placed in front of the mirror, is even sufficient to produce the rings; but in that case only part of their circumference is seen.

The rings formed by diffused light may be viewed directly without being projected on a screen. Stokes places a candle in the centre of curvature of the mirror with tarnished surface, so that the image of the candle may coincide with it, and places the eye at some distance beyond the centre; beautiful rings are then seen formed in the air. Quételet places a candle near the eye, at about a yard from a plane mirror with tarnished surface, so that the candle and its image may seem to coincide; he thus obtains portions of coloured rings round the image of the candle. Herschel receives a beam of solar light on a concave spherical metallic mirror, and intercepts the reflected beam by a screen; by then forming a cloud of dust in the air in front of the mirror, he obtains coloured rings of considerable brightness.

There are several other ways in which coloured rings and fringes may be formed by diffused light, but we must refer, for the description of these and for the more detailed explanation of the phenomena, to works specially devoted to light. (See Daguin, *Traité de Physique*, iv. 463.)

Composition of Colours.

Colours are either simple or compound. The simple colours are those of a pure spectrum, formed either by refraction through a prism, or by diffraction through a grating (p. 606); and compound colours are produced by the mixture of two or more of these simple colours, as in the instance of Newton's rings, or the fringes produced by diffraction. Compound colours may be similar to the pure colours of the spectrum, but are rarely identical with them in the impression which they produce on the visual organs. The resultant tint, produced by the mixture or superposition of any number of simple colours, may be investigated by one of the following methods:

1. By mixing coloured substances in fine powder, This method, however, yields only dull and deadened colours, in consequence of the large quantity of light absorbed; moreover, the rays reflected from the surfaces of the two substances are mixed with rays which have penetrated to a certain depth, and have been there reflected, so that the tint which would be produced by the mixture of the rays directly reflected from the surface is modified by colours arising from absorption.

2. By covering with black paper certain portions of a revolving disc, tinted with the colours of the spectrum (p. 619), the colour perceived being that which is produced by the composition of the remaining spectral colours.

3. By tinting two pieces of paper with the colours whose composition is to be studied, laying them on a black table, setting up between them a plate of unsilvered glass, and placing the eye so that the image of one of them seen by reflection may coincide with that of the other seen directly through the glass (Helmholtz).

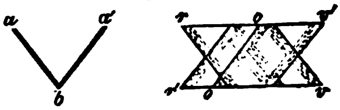
This and the second method are preferable to the first, the only source of error affecting them being the deviation of the artificial colours from the pure tints of the spectrum. The only way of attaining perfectly accurate results is to operate directly on the rays of the spectrum itself, as in the following methods:

4. By intercepting some of the coloured rays as they emerge from the prism, and bringing the rest to a focus by an achromatic lens.

5. By receiving the rays of the spectrum on a row of plane mirrors, capable of being adjusted so as to reflect any required rays to the same point on a screen.

6. *Helmholtz's method* (Ann. Ch. Phys. [3] xxxvi. 500). This method, which is the most exact of all, consists in viewing, through a vertical prism, two narrow slits, *ab*, *a'b*, forming a right angle (fig. 672), and each inclined 45° to the edge of the prism. The prism being placed about four yards from the slits, and in the position of least deviation, two spectra *r v*, *r' v'*, are seen, in which, with the aid of a telescope, the principal fixed lines may be distinguished parallel to the slits. These two spectra are partly superposed, and the dimensions of the slits must be such that each coloured band *o o* of one spectrum shall cross all the coloured bands of the other.

Fig. 672.



To find the effect produced by the combination of two colours, the telescope is directed so that the intersection of its cross-wires is projected on the combination to be examined, and the eye is placed behind a small hole in a screen, at 50 or 60 centimetres from the telescope, so that it may perceive only a very small space around the point of intersection. The compound tint required may thus be examined without being affected by the neighbouring colours. By then covering up the two slits successively, the simple colours which have produced the combination may be seen.

In order to vary the relative quantities of light in the component colours, the prism was inclined in such a manner as to bring it more nearly parallel with one of the slits. The spectrum of this slit was thereby brought nearer to the rectangular form, and its colours were more condensed, while the contrary effect was produced upon those of the other. By adding a third slit, the effect of combining three colours may be observed. By these means Helmholtz has obtained the following results:

1. The compound tint formed by the mixture of two simple colours is sometimes identical with a simple colour of the spectrum, but in many cases it is different from them all: for example, the greenish-yellow and greenish-blue of the spectrum form a green much darker than that of the spectrum. This last green, as well as the violet and red of the spectrum, cannot be imitated exactly by the mixture of any other colours. 2. The colour produced by the union of three simple colours is different from that which would be obtained by combining one of them with a simple colour of the spectrum, similar to that which results from the combination of the other two. For instance, the red and bluish-green of the spectrum form *yellow*; but red, with the bluish-green produced by the union of green and indigo, forms *white*. 3. There are many combinations of three colours which form white. 4. With three colours only it is not possible to obtain satisfactory imitations of all the colours of the spectrum, the number of simple colours required for the purpose being at least five, viz., *red*, *yellow*, *green*, *blue*, and *violet*. Hence, according to Helmholtz, the theory of three primary colours (p. 640) does not rest on a satisfactory foundation; and if it is possible to obtain something like an imitation of all the spectral colours by the mixture of three coloured powders, the result must be attributed partly to the want of brightness in the colours used, partly to the circumstance that the resulting compound colours have not generally been directly compared with the colours of the spectrum, from which, in most instances, they differ considerably. The three colours hitherto adopted, viz., *red*, *blue*, and *yellow*, are not even the three best adapted to the purpose; better results are obtained with red, green, and violet, but even then the imitations are far from perfect. For the contrary results obtained by Maxwell, from which it appears that all colours whatever may be produced by the combination of three primary colours, see page 650.

Complementary colours.—This name was applied by Newton to any two colours which by their mixture produce white light; such are *green* and *red*; *orange* and *blue*; *yellow* and *violet*.

Every colour, whether simple or compound, has its complementary colour; moreover, every colour has an infinity of complementary colours, inasmuch as if either of the colours be mixed with white in any proportion, the two will still form white by their union.

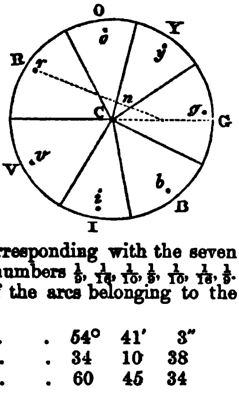
Helmholtz has made some remarkable experiments on complementary colours by throwing the pure spectrum, formed by a prism and achromatic lens, on a screen pierced with two narrow slits parallel to the edges of the prism, and capable of being brought close together at pleasure. The two homogeneous coloured pencils thus obtained are received on a lens which condenses and brings them to a single focus on a white screen placed at a suitable distance. By this mode of experimenting, Helmholtz has shown that there exists an infinity of binary groups of colours, which, when united in *due proportion*, produce a perfect white. With the exception of pure green, every simple colour of the spectrum is complementary of another simple colour.

By varying the breadth of one of the slits, the relative intensities of the two coloured beams could be altered, and it was thus found that the proportions between the intensities of two coloured beams which produce white light by their combination sometimes varies with the intensity of the incident light. This is shown by the following numbers:

Group of complementary colours.	Ratio of intensity of the second colour to the first.	
	Bright light.	Faint light.
Violet—greenish-yellow	10	5
Indigo—yellow	4	3
Blue—orange	1	1
Greenish-blue—red	0·44	0·44

The same mode of experimenting led to the unexpected conclusion that the mixture of the *blue* and *yellow* rays of the spectrum produces white, whereas the mixture of blue and yellow liquids or powders always produces green. This result is confirmed by painting two paper discs, one with chromate of lead or gamboge, the other with cobalt-blue, and making the reflected image of the one coincide with or overlap the direct image of the other, as in method 3 (p. 648). The compound image thus seen is white. With the yellows above mentioned and artificial ultramarine, the white has a slight reddish tinge; with Prussian-blue, a greenish tinge. The production of green by the mixture of blue and yellow powders or liquids, arises from partial decomposition of the light by absorption, as explained at p. 647.

Fig. 673.



Newton's construction for the calculation of composite colours.—The following geometrical construction was given by Newton for calculating approximately the result of mixing a number of simple colours. The circumference of a circle (*fig.* 673) is divided into seven parts corresponding with the seven principal colours of the spectrum, and proportional to the numbers $\frac{1}{9}, \frac{1}{16}, \frac{1}{10}, \frac{1}{9}, \frac{1}{10}, \frac{1}{16}, \frac{1}{9}$. A simple calculation then gives the following lengths of the arcs belonging to the several colours:

Red . . .	60°	45′	34″	Blue . . .	54°	41′	3″
Orange . . .	34	10	38	Indigo . . .	34	10	38
Yellow . . .	54	41	1	Violet . . .	60	45	34
Green . . .	60	45	3				

The centres of gravity of each of these arcs *r*, *o*, *y*, *g*, *b*, *i*, *v*, are then marked; and to obtain the resultant of the mixture of several colours, forces proportional to the quantities of the colours to be mixed are supposed to be applied to the centres of gravity of the corresponding arcs, and the point of application of the resultant of these forces is determined. The colour sought will be that of the arc of the sector in which this point of application falls. Thus, to find the result of mixing red, blue, and yellow rays whose intensities are to one another as the numbers n_r, n_b, n_y, we must seek the point of application of the resultant of three parallel forces proportional to n_r, n_b, and n_y, applied at the points *r*, *b*, *y*. If this point falls at *n*, the mixture will be yellow, inclining to green, because the point *n* is nearer to the limit of the green than to that of the orange. The nearer the point *n* is to the centre C, the more will the resulting colour be mixed with white; if it coincides exactly with C, the mixture will be white, as, for example, when the seven colours are combined in quantities proportional to the arcs which represent them, the resultant being then applied at the centre of gravity C of the entire circumference.

It follows from Newton's rule: 1. That two simple colours following one another on the circumference produce by their mixture an intermediate tint; an exception must however be made with regard to red and violet, which do not follow one another in the spectrum. 2. Two colours separated by a third, yield that third by their mixture; thus red and yellow yield orange, orange and green yield yellow, &c. Indigo and red, which are nearly at the opposite extremities of the spectrum, yield a reddish colour different from violet.

Biot has reduced Newton's method to a general formula. For this purpose he calculates the co-ordinates of the centres of gravity of the arcs, taking as the axis of abscissæ the straight line passing through the point of separation of the arcs corresponding to the violet and red, and through the centre, taken as the origin of co-ordinates; he then multiples each co-ordinate by the number of rays of the corresponding colour which is to enter into the compound, divides the sum of the products by the sum of the rays which are to be compounded, and thus obtains the co-ordinates of the point of application of the resultant. Designating the number of rays of each colour by the initial letter of its name, these co-ordinates are:

$$X = \frac{0{\cdot}82284\,(r+v) + 0{\cdot}207398\,(o+i) - 0{\cdot}513992\,(y+b) - 0{\cdot}353796\,v}{r+o+y+g+b+i+v.}$$

$$Y = \frac{0{\cdot}48235\,(r-v) + 0{\cdot}963163\,(o-i) + 0{\cdot}813736\,(y-b)}{r+o+y+g+b+i+v.}$$

These co-ordinates give the distance D, of the point of application of the resultant from the centre of the circle, as well as the angle α, which the line joining these points makes with the axis of x: for $\tan\alpha = Y : X$; and $Y = D \sin\alpha$, or $X = D \cos\alpha$.

The value of α shows in which particular sector the point of application falls, and the ratio $D : 1 - D$ shows the proportion of simple light and white light composing the resulting colour.

The preceding method was given by Newton as an empirical rule for representing the results which he obtained by forming compound colours containing given proportions of simple light at the focus of a lens. It cannot be regarded as more than a rough approximation, and is, indeed, less exact than Newton supposed: we have seen, for example, that the mixture of blue and yellow rays may produce white instead of green.

A more satisfactory method of calculating the composition of colours has been given by **Maxwell** (Phil. Mag. [4] xiv. 40; Proc. Roy. Soc. x. 404), from whose observations it appears that the colours of the spectrum, as laid down according to Newton's method from actual observation, lie, not in the circumference of a circle, but in the periphery of a triangle, showing that all the colours of the spectrum may be *chromatically* represented by three, which form the angles of the triangle. The wave-lengths and positions in the spectrum of these three primary colours are:

	Wave-lengths in millionths of an inch.
Scarlet .	2328—about one-third from line C to D.
Green .	1914—about one-quarter from E to F.
Blue . .	1717—about half-way from F to G.

This form of the diagram of colour, as perceived by the human eye, is in accordance with Young's theory of *three primary sensations* of colour, which are excited in different proportions, when different kinds of light enter the eye. According to this theory, the threefold character of colour, as perceived by us, is due, not to a threefold composition of light, but to the constitution of the visual apparatus, which renders it capable of being affected in three different ways, the relative amount of each sensation being determined by the nature of the incident light. If we could exhibit three colours corresponding to the three primary sensations, each colour exciting one and one only of these sensations, then, since all other colours whatever must excite more than one primary sensation, they must find their places in Newton's diagram within the triangle of which the three primary colours form the angles.

If this theory be true, the complete diagram of all colour, as perceived by the human eye, will have the form of a triangle. The colours corresponding with the pure rays of the spectrum must all lie within this triangle, and all colours in nature being mixtures of these, must lie within the line formed by the spectrum. If, therefore, any colours correspond with the three primary sensations, they will be found at the angles of the triangle, and all the others will be within the triangle.

The other colours of the spectrum, though excited by undecompounded light, are compound colours; because the light, though simple, has the power of exciting two or more colour-sensations in different proportions—as, for instance, a blue-green ray, though not compounded of the blue rays and green rays, produces a sensation compounded of those of blue and green.

The three colours found by experiment to form the three angles of the triangle, and Newton's diagram, *may* correspond with the three primary sensations.

A different geometrical representation of the relations of colour may be thus described:—Take any point not in the plane of Newton's diagram; draw a line from this point as origin through the point representing a given colour in the plane, and produce it, so that the length of the line may be to the part cut off by the plane, as the intensity of any given colour is to that of the corresponding point in Newton's diagram. In this way, any colour may be represented by a line drawn from the origin, whose direction indicates the quality of the colour, and whose length depends on its intensity. The resultant of two colours is represented by the diagonal of the parallelogram formed on the lines representing the colours.

Taking three lines from the origin through the points of the diagram corresponding with the three primaries as axes of co-ordinates, any colour may be expressed as the resultant of definite quantities of each of the three primaries, and the three elements of colour will then be represented by three dimensions of space.

The method of observation by which the preceding conclusions are established consists in selecting three colours of the spectrum, and mixing them in such proportions as to be identical in colour and brightness with a constant white light. Three standard colours being assumed, and the quantity of each required to produce the given white having been found, the quantities of two of these, combined with a fourth colour which will produce the given white, are then determined. A relation is thus obtained between the three standards and the fourth colour, whence its position in Newton's diagram, with reference to the three standards, may be laid down.

The instrument employed in the experiment consists of a dark chamber about 5 feet long, 9 inches broad, and 4 deep, joined to another 2 feet long, at an angle of about 100°. Light admitted by a narrow slit at the end of the shorter chamber, falls on a lens, and is refracted through two prisms in succession, so as to form a pure spectrum at the end of the long chamber. Here there is placed an apparatus consisting of three movable slits, which can be altered in breadth and position, the position being read off on a graduated scale, and the breadth ascertained by inserting a fine wedge into the slit till it touches both ends.

When white light is admitted at the shorter end, light of three different colours is refracted to the three slits. When white light is admitted at the three slits, light of these three kinds in combination is seen by an eye placed at the slit in the shorter arm of the instrument. The white light employed is that of a sheet of white paper placed on a board and illuminated by the sun's light in the open air, the instrument being in a room and the light moderated where the observer sits.

Another portion of the same white light goes down a separate compartment of the instrument, and is reflected at a surface of blackened glass, so as to be seen by the observer *in immediate contact* with the compound light which enters the slits and is refracted by the prisms.

Each experiment consists in altering the breadth of the slits till the two lights seen by the observer agree both in colour and in brightness. In this way the relative places of sixteen kinds of light were found by two observers, both of whom agreed in finding the positions of the colours to lie very close to the two sides of a triangle, the extreme colours of the spectrum forming doubtful fragments of the third side.

The chromatic relations between these sixteen colours being thus ascertained, the next step is to ascertain the positions of these colours with respect to Fraunhofer's lines. This is done by admitting light into the shorter arm of the instrument through the slit which forms the eye-hole in the former experiments. A pure spectrum is then seen at the other end, and the position of the fixed lines is read off on the divided scale. In order to determine the wave-lengths of each kind of light, the incident light was first reflected from a stratum of air too thick to exhibit the colours of Newton's rings. The spectrum then exhibited a series of dark bands at intervals increasing from the red to the violet. The wave-lengths corresponding with these form a series of submultiples of the retardation; and by counting the bands between two of the fixed lines, whose wave-lengths have been determined by Babinet (p. 607), the wave-lengths corresponding with all the bands may be calculated; and as there is a great number of bands, the wave-lengths become known at a great many different points. In this way, the wave-lengths of the colours compared may be ascertained, and the results obtained by one observer rendered comparable with those of another.

Another instrument, invented by Maxwell for comparing combinations of colour, is the "colour-top," which is a spinning-top, having its flat upper surface divided into two concentric circles, each circle being further divided into sectors, which can be covered with different coloured papers. When the top is spun, the colours in each of the circles produce mixed tints, and the proportions of those in the outer circle are varied till the mixed tint matches that produced by a given combination in the inner circle, the proportions being measured by a graduation on the circumference.

Nomenclature of Colours.—The terms employed to designate different shades of colour are for the most part very indefinite, being sometimes borrowed from natural objects or substances, sometimes from the names of inventors of preparations which exhibit the particular colour, and from various other sources more or less fanciful. The colours of minerals are usually distinguished by comparison with familiar natural objects which they more or less resemble: thus blues are specially distinguished as azure, violet, lavender, smalt, indigo- and sky-blue; greens as verdigris, celandine, mountain, leek, emerald, apple, grass, asparagus, olive, oil, and siskin green; yellows as sulphur, straw, wax, honey, lemon, ochre, wine, cream, and orange-yellow; reds as aurora or roseate, hyacinth, brick, scarlet, blood, flesh, carmine, rose, crimson, peach-blossom, columbine, and cherry-red; browns as clove, hair, broccoli, pinchbeck, wood, and liver-brown; greys as pearl, smoke, and ash-grey.

To obtain greater accuracy in the nomenclature of colours, Chevreul has devised the following scheme (*De la loi du contraste simultané des couleurs*, p. 87): In the first place he assigns definite meanings to the terms tint (*nuance*), and shade, or tone (*ton*), denoting by tint the result of mixing pure colours in various proportions, and by shade or tone the result of mixing any tint or simple colour with black or white, so that each tint is susceptible of an infinite gradation of shades. A tint is weakened or *lowered* by the addition of white, strengthened or *heightened* by addition of black. Colours mixed with black are said by painters to be deadened (*rabattues*), they then reflect less light; in fact, if a coloured surface be less and less illuminated, it becomes continually darker and ultimately black. This effect is experienced at the close of day, all the colours then becoming darker and turning towards black.

Chevreul's Chromatic Circle.—Chevreul has formed a table of 72 tints passing gradually one into the other, and each modified by 20 shades, some produced by admixture of white in various proportions, the rest by admixture of black. Imagine a circle divided into 72 equal sectors. Three equidistant sectors are coloured respectively with *red*, *yellow*, and *blue*, and at equal distances from these three colours are placed those which result from their mixture two by two, viz. *orange* between red and yellow, *green* between yellow and blue, *violet* between red and blue; then between these six tints are placed the intermediate tints, and so on till the whole 72 are complete. Each of these 72 sectors is then divided into quadrangular segments by 20 concentric circles, and in the segments thus formed are placed the shades belonging to each colour. At the centre is a small white circle, starting from which each tint becomes gradually deeper by the continual abstraction of white, till the pure tint is reached, and beyond this the shade is continually deepened by addition of black till the circumference is reached, which is quite black. There is therefore a circular series of segments containing the pure tints with their maximum of intensity, and starting from these, the shades in each sector become weaker towards the centre, stronger towards the circumference. The series of colours contained in any one sector forms a gamut of shades of the corresponding tint. Each circle of segments contains the 72 tints corresponding with the shade of that circle. We have thus a diagram of 1440 colours forming types near enough to one another for the requirements of the arts. It would be useful also to add the gamut of white, that is to say, the series of grey shades from white to black. Such a diagram constructed with permanent colours, on painted porcelain for example, is capable of rendering important service in the arts, by affording a standard nomenclature of colours, which may be designated by the numbers of the sector and the circumference in which they occur.

Lecocq arranges the coloured segments in a different way. He divides the surface of a sphere into quadrangular spaces by means of meridians and parallels. The pure colours are placed at the equator, and each of them becomes darker along the course of its meridian towards one pole, at which there is a black spot, and lighter towards the other pole, where there is a white spot. It would be more convenient to use a cylinder, having one of its bases bordered with black, the other with white, and the pure colours arranged round a zone in the middle. The cylinder might also be developed on a plane, and the whole series of tints and shades thus presented to the eye at once. By repeating at one end of the diagram thus formed, some of the gamuts from the opposite end, each gamut will be placed next to those which differ from it the least. In this form the diagram is more easily constructed, especially if it is to be made in porcelain.

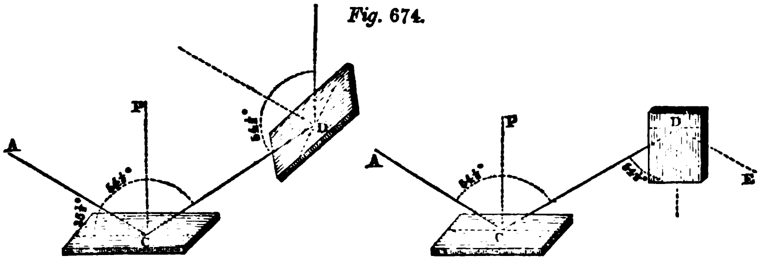
Polarisation and Double Refraction.

When a beam of light proceeding from a self-luminous source traverses a homogeneous medium without encountering any obstacle, it exhibits the same properties on all sides,—on the north, south, east, and west, for example, if we suppose it to be vertical. The light composing such a beam is called *ordinary* or *natural light*. But after the light has met with any obstacle, and has consequently undergone reflection or refraction, it exhibits, for the most part, different properties on different sides. If, for example, the beam of light be received obliquely on a glass mirror, and the mirror be turned round it, taking care not to alter the angle of incidence, the intensity of the reflected beam will vary according to the side of it which is presented to the mirror. A ray thus modified is said to be polarised. The properties of polarised rays all relate to changes of intensity or modifications of colour, and never affect the direction in which they are reflected or refracted.

Light may be polarised in either of the following ways:—

1. *By Reflection from the surface of transparent media.*—Suppose a ray of light AC (*fig.* 674) to fall upon a plate of glass (not silvered, but blackened at the lower surface) at C, making an angle of 54½° with the normal PC, or 35½° with the reflecting surface. This ray will be reflected in the direction CD, making an angle PCD = ACP, and in the same plane as AC and CP. Now suppose the reflected ray to fall upon a second surface of glass at the same angle of 54½° with the normal. If, then, the second mirror be so placed, that its plane of reflection is parallel to the plane of reflection from the first surface (see left-hand figure), then the ray will be reflected from the second surface in the direction DE, just as if it proceeded directly from a luminous source, and had not undergone previous reflection; but if the second mirror be so adjusted that its plane of reflection is perpendicular to that of the first (see right-hand figure), then the ray CD will not be reflected from it at all, or at least the intensity of the reflected beam will be comparatively small. In intermediate positions, still at the same angle of incidence, the ray CD will be partially reflected, the quantity of light in the reflected ray DE being greater as the planes of reflection of the two mirrors are more nearly parallel.

Fig. 674.

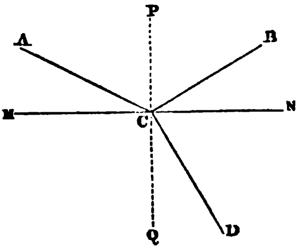


The ray, after reflection from glass at an angle of 54½°, appears then to exhibit different properties, according to the direction in which it is a second time reflected, being in fact reflexible in different degrees at different azimuths; it is therefore *polarised.*

The plane in which a polarised ray is most easily reflected is called the **plane of polarisation**; it coincides with the plane of reflection (or of incidence).

The angle 54½° is called the **polarising angle** for glass. For every medium there is a particular polarising angle, the magnitude of which depends upon the refracting power of the medium, according to the following law, discovered by Brewster: *The polarising angle* ACP (*fig.* 675) *is that for which the refracted ray* CD *is perpendicular to the reflected ray* CB. Now let μ denote the index of refraction, then $\mu = \frac{\sin ACP}{\sin QCD}$; but the angle ACP = BCP [$= \theta$]; and since BC is perpendicular to CD, and QC to CN, angle QCD = BCN = 90° − θ; therefore, $\mu = \frac{\sin\theta}{\cos\theta} = \tan\theta$; that is to say, *the polarising angle is the angle whose tangent is equal to the index of refraction.*

Fig. 675.



The following table exhibits the polarising angles of a few transparent substances, chiefly according to the observations of Biot and Arago:—

Name of substance.	Polarising angle.		Name of substance.	Polarising angle.	
	Measured from normal.	Measured from surface.		Measured from normal.	Measured from surface.
Fluor spar . .	54° 50′	36° 10′	Topaz . . .	58° 40′	31° 20′
Water . . .	52 45	37 15	Iceland spar .	58 23	31 37
Glass . . .	54 35	35 25	Spinel ruby .	*60 16	29 44
Obsidian . .	56 03	33 57	Zircon . . .	*63 08	26 52
Selenite . . .	56 28	33 32	Sulphur (native) .	*64 10	25 50
Amber . . .	56 35	33 25	Antimony-glass .	*64 45	55 15
Rock-crystal . .	57 22	33 38	Chromate of lead .	*67 42	22 18
Sulphate of barium	58 0	32 0	Diamond . . .	*68 02	21 58

There are but few substances capable of completely polarising light by reflection, and generally speaking the polarising power is least in those media which have the largest indices of refraction. According to Brewster, it is only those media whose refractive index is less than 1·7, which are capable of polarising completely; such are those not marked with an asterisk in the preceding table. But even when the index is less than 1·7, the polarisation is never complete, if the beam of light is bright. In general, substances which reflect but little light, polarise a large proportion of it. Metals, with clean and polished surface, polarise scarcely at all. In all cases, however, Brewster's law applies to the incidence at which the reflected beam contains the largest proportion of polarised light.

As the several coloured rays have different indices of refraction, it is evident that only homogeneous light can be completely polarised by reflection. Solar light, or ordinary gas or candle light, can never be made to disappear completely in the manner above described. In fact, with media of high dispersive power, such as oil of cassia, diamond, chromate of lead, or specular iron, all the colours of the spectrum may be successively brought into view by slightly altering the inclination of the reflecting surface in the vicinity of the polarising angle. With glass and water, in which the angles of polarisation for the extreme rays of the spectrum do not differ by more than 15′ or 20′, the colours are less perceptible; nevertheless the light never disappears entirely, and always exhibits a slight coloration after the second reflection.

Light is more or less polarised by reflection at all angles of incidence, excepting perpendicular incidence, the proportion of polarised light in the reflected beam being greater as the angle of incidence differs less from the polarising angle determined by Brewster's law.

If a ray, partially polarised by reflection at any angle differing from the polarising angle, be again reflected from the same medium at the same angle, the proportion of polarised light in it will be increased; and by a number of successive reflections, the ray may be brought indefinitely near to the state of complete polarisation, the number of reflections required for the purpose being less as the angle of reflection differs less from the polarising angle.

2. *By ordinary Refraction.*—When light passes from one medium to another, the refracted ray is polarised as well as the reflected ray, its plane of polarisation being perpendicular to the plane of refraction, or of incidence, and, therefore, also to the plane of polarisation of the reflected ray. The refracted ray will therefore be reflected from a surface of glass at an angle of 54½°, just under the circumstances in which the ray polarised by reflection would not. Light, however, is never completely polarised by one refraction; but the proportion of polarised light in the refracted beam is greater as the angle of incidence is nearer to the polarising angle; and by successive refractions through a number of surfaces of glass, or other medium, it may be brought within any assigned limit of complete polarisation. A bundle of thin plates of glass or mica, bound together in a frame, forms a very convenient apparatus for polarising light, whether by refraction or by reflection.

3. *By Double Refraction.*—All crystalline bodies not belonging to the regular system, possess the power of double refraction; that is to say, a ray of light entering such a medium is split up into two rays of equal intensity, which traverse the crystal in different directions. In all such media, however, there are either one or two directions in which double refraction does not take place, and these lines are called the optic axes of the crystal. Transparent calcspar, or Iceland spar, which crystallises in rhombohedrons, and exhibits double refraction more distinctly than any other substance, is a crystal with one optic axis, the direction of that axis being parallel to the line joining the obtuse summits of the rhomb. A ray traversing the crystal in a direction parallel to this axis is not divided into two; but in all other directions the ray is doubly refracted; and the two rays into which it is thus divided are both completely polarised, the plane of polarisation of the one being parallel to the *principal section* of the crystal, that is to say, a plane passing through the optic axis and the direction in which the ray traverses the crystal; the other in a plane at right angles to that section. The ray which is polarised in the principal section follows the ordinary laws of refraction, remaining always in the plane of incidence, and having for all incidences a constant index of refraction; but the ray polarised perpendicularly to the principal section follows different laws of refraction, its direction not being confined within the plane of incidence, unless that plane coincides with or is perpendicular to the principal section, and its index of refraction, excepting in the last-mentioned case, varying continually with the angle of incidence. The former of these rays is called the *ordinary*, the latter the *extraordinary* ray. The mode of refraction of the latter will be more fully explained hereafter.

When these two oppositely polarised rays, which have traversed a rhomb of Iceland spar, fall on a plate of glass at the angle of 54½°, so placed that the plane of reflection is parallel to the principal section of the crystal, the ordinary ray is reflected, and the extraordinary ray is not, the contrary effect taking place when these planes are at right angles to each other. When the plane of reflection is inclined to the principal section at any angle between 0° and 90°, both rays are reflected, but with different intensities.

The two polarised beams, on emerging from the crystal, will overlap each other, or will be completely separated, according to their breadth and the thickness of the crystal. When, however, it is desired to examine only one of them, it is most convenient to throw the other completely out of the field of view. This may be effected in one of the following ways:

α. *By Reflection.*—The apparatus for this purpose, called a **Nichol's prism**, consists of two similar prisms of calcspar (*fig.* 676), ABCD, CDEF, cemented together with Canada balsam at the faces CD. The faces AB, EF are cut so as to make an angle of 68° with the obtuse edges AE, BF of the natural crystal (the natural faces make an angle of 71° with the obtuse edges), and the faces CD are perpendicular to AB and EF. With this arrangement, it is found that of the two rays, *no*, *ne*, into which an incident ray, *mn*, is divided, the ordinary ray, *no*, on reaching the surface of Canada balsam (whose index of refraction is less than that of the ordinary, and greater than that of the extraordinary, ray), suffers total reflection in the direction *op*, while the extraordinary ray passes on in the direction *ef*, and emerges in *fg*, parallel to *mn*. An eye placed at *f*, therefore, sees but one image, viz. that formed by the extraordinary ray. Hence, a beam of ordinary light passing through it will be polarised in a plane perpendicular to the principal section—that is to say, to the shorter diagonal of the rhomb, *ab* (*fig.* 677); and a ray, already polarised, will be stopped by the prism if its plane of polarisation is parallel to *ab*, but will pass freely through it when the plane of polarisation is perpendicular to *ab*, or parallel to the longer diagonal *cd*. Hence, also, two Nichol's prisms, placed one behind the other, appear perfectly opaque when their principal sections are at right angles to each other, perfectly transparent when the principal sections are parallel, and transmit light with diminished intensity in intermediate positions.

Fig. 676.

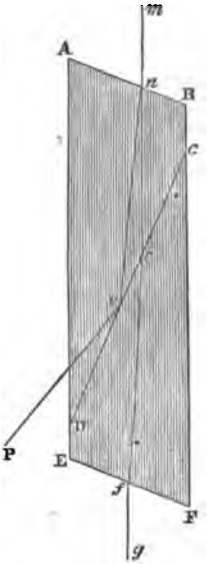
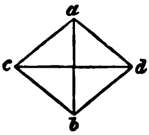


Fig. 677.



β. *By Absorption.*—Certain double-refracting crystals, especially the **tourmaline**, have the power of transmitting light only when polarised in a particular direction with regard to their optic axes. The tourmaline forms crystals belonging to the hexagonal system, having one optic axis parallel to the axis of figure, and transmitting light only when polarised in a plane perpendicular to the optic axis. Hence, when a ray of light polarised by reflection from glass at the angle of 54½°, is viewed through a plate of tourmaline cut with its faces parallel to the optic axis, then if the crystal be held with its optic axis perpendicular to the plane of reflection, the ray will pass through it as freely as its colour will permit; but if the tourmaline be held with its axis parallel to the plane of reflection, the reflected rays will be completely absorbed, and no light will pass. If the tourmaline be gradually turned round from the first position to the second, the quantity of light which passes through it will continually decrease, because the polarised ray is then divided by the tourmaline into two, one polarised at right angles to the axis, the other parallel thereto, the intensity of the former continually decreasing, and that of the latter increasing as the tourmaline is turned round. When a ray of ordinary light is transmitted through a tourmaline plate of a certain thickness, cut as above described, it is divided into two, as by other double-refracting crystals; but the ordinary ray is completely absorbed, and only the extraordinary ray passes through, so that the emergent beam is completely polarised in a plane perpendicular to the axis of the tourmaline. Hence if two such plates of tourmaline be superposed, and the light of the sky be viewed through them, then if the two be placed with their optic axes parallel, the light will pass through them as freely as their colour and imperfect transparency will permit; but if one of the tourmalines be then turned round, the quantity of light transmitted will decrease as the axes deviate more and more from parallelism, and at last, when the two axes cross one another at right angles, the light will be completely intercepted.

Two such tourmalines mounted with their faces parallel to each other, and so as to permit one of them to revolve in the plane of the axis, form a very convenient and portable apparatus for experiments on polarised light. A single tourmaline is also very convenient for examining light polarised by reflection or refraction. The only objection to the tourmaline is its colour, the best polarising tourmalines having always a brown colour, which greatly modifies the colour of the transmitted light, especially as, in order that the tourmaline may polarise completely, it must have a thickness of at least the tenth of an inch.

There are a few other double refracting crystals possessing similar properties; in particular the so-salled "sulphate of iodo-quinine," discovered by Dr. Herapath. This substance crystallises in thin six- or eight-sided plates, which are transparent and nearly colourless by transmitted light when viewed separately; but when two of them are superposed, with their longer dimensions crossing one another at right angles, the part where they cross appears quite black, even if the thickness of the crystals does not exceed $\frac{1}{20}$ of a millimetre. The crystals of this compound may therefore be used in the same manner as tourmalines, and are even better adapted for optical use, by their greater transparency and freedom from colour; but their fragility renders it somewhat difficult to manipulate with them.

The best substitute for a tourmaline is the Nichol's prism, above described. The calcspar crystals being perfectly colourless and very transparent, transmit much more light than two superposed tourmalines.

All arrangements for examining the properties of polarised light necessarily consist of two parts; viz., the polariser, by which the light is brought into the polarised state, and the analyser, by which its state of polarisation and its properties are examined; thus, when a ray is reflected from a plate of glass at an angle of 54½°, and the reflected beam examined by a tourmaline held before the eye, the plate of glass is the polariser, and the tourmaline the analyser. It is clear that any one of the apparatus above described, namely a reflector, a refractor, a double-refracting crystal, a tourmaline, or a Nichol's prism, may be used either as polariser or analyser.

Nature of Polarised Light.—The existence of rays having different properties on different sides was regarded by Newton as a decisive objection against the wave-theory of light, on the ground that pressures or movements excited by a luminous body in an elastic medium ought to be equal in all directions; and Huyghens was obliged to admit his inability to account for the existence of polarised rays on the undulatory theory as then understood. The reason of this apparent inability of the wave-theory to explain the phenomena of polarisation, was that, at the time of which we are speaking, the vibratory movements of the ether were supposed to take place wholly in the direction of propagation of the waves, and on that hypothesis it is impossible to conceive of rays of light, any more than rays of sound, possessing different properties on different sides. But later experimental researches, and the investigation of the subject on the principles of analytical mechanics, have shown that the vibrations of the luminiferous ether take place in planes tangential to the wave-surface, or transversely to the direction of the ray. From this point of view, the difference between ordinary and polarised light is easily explained. An ordinary or natural ray is one in which the vibrations take place in all directions successively in the plane of the wave; and a polarised ray is one in which the vibrations, still tangential to the wave-surface, are confined to one plane. Suppose, for example, the direction of the ray to be vertical, or that of the wave-surface horizontal; then, if the ray be polarised, the direction of vibration of all the particles will be either north and south, or east and west, or in some one intermediate azimuth; and if it be unpolarised, the vibrations will take place in all these directions successively.

This view of the nature of polarised light is established by the experiments of Fresnel and Arago on the interference of polarised rays, the general result of which is, that *two rays whose planes of polarisation* (p. 653) *are parallel to one another interfere just like unpolarised rays: but two rays whose planes of polarisation are perpendicular to one another do not exhibit any phenomena of interference, whatever may be their difference of phase.* These results are easily conceivable if the vibrations are transverse to the direction of the ray; for if the vibrations of the two rays take place in directions parallel to each other, the resultant will be equal to the sum or difference of their individual movements, as explained at page 598, and will be reduced to zero, that is to say, the rays will destroy each other, when their phases are exactly opposite; but if their vibrations are performed in planes inclined to one another at any angle, there will be, at every point, a finite resultant, determined in magnitude and position by the rule of the parallelogram of velocities, and never becoming equal to nothing. Hence, two rays whose planes of polarisation are not parallel, can never interfere so as to produce complete darkness; and if their planes are at right angles to one another, they cannot interfere at all. If, on the other hand, the vibrations of the ether take place in the direction of the ray, it is impossible to conceive any conditions which would prevent them from interfering with one another, and producing darkness when they meet one another under a certain difference of phase.

The experiments which show that the interference of polarised rays does depend, as above described, on their state of polarisation, are the following:

1. The light passing through two narrow parallel slits very close together, as in Young's experiment (pp. 599, 604), is polarised by covering the slits with two pieces of the same plate of tourmaline, cut parallel to the axis, which polarises the light in a plane perpendicular to that axis. If the two tourmaline plates have their axes parallel to one another, the two beams of light interfere and produce fringes, just as if the tourmalines were not there; but if they are placed with their axes at right angles to one another, all the fringes disappear. In intermediate positions of the tourmalines fringes are produced, but fainter as the angle between the axes approaches more nearly to a right angle. Instead of tourmalines, two small bundles of mica-plates may be placed before the slits, in a position inclined to the direction of the rays, which are then, after transmission, almost wholly polarised in a plane perpendicular to the plane of incidence. The fringes then disappear when the bundles of plates are so placed that the two planes of incidence are at right angles to each other.

2. The two slits are covered with two fragments of the same plate of calcspar or rock-crystal, cut parallel to the optic axis. Each plate then gives an ordinary and an extraordinary ray, whose planes of polarisation are at right angles to one another. If the axes of the two fragments are parallel, the two ordinary rays which emerge from them produce fringes, just as if they were unpolarised; so likewise do the two extraordinary rays, and these two systems of fringes are superposed. If now one of the crystalline plates be gradually turned round in the plane parallel to its axis, the fringes become fainter, and when the axes of the two plates are at right angles to one another, the fringes disappear altogether, and give place to uniform light. At the same time, however, other systems of fringes make their appearance on the sides, being produced by the interference of the ordinary rays proceeding from one of the slits with the extraordinary rays from the other; they are shifted to the sides on account of the difference of velocity of the ordinary and extraordinary rays within the crystal. So long as the axes of the two plates remain parallel, the ordinary ray of the one and the extraordinary ray of the other are polarised in planes at right angles to one another, and the lateral fringes are not produced; but on inclining the axes to one another, these lateral fringes appear, becoming more and more brilliant as the angle between the axes increases, and attaining their greatest brightness when the two axes form an angle of 90°.

3. When a narrow screen, such as a hair, is placed in the path of the two rays issuing from a rhomb of Iceland spar, placed before the focus of a lens, no fringes are produced within the shadow, as they would be by ordinary light, because the two rays are polarised in planes at right angles to one another.

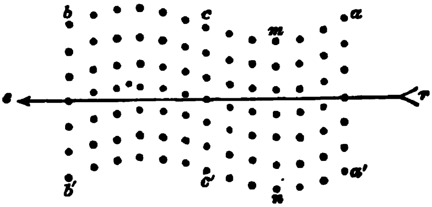
In Fresnel's mirror experiment (p. 599), the rays are polarised by reflection in the same plane; and in that of Young (p. 602), the rays originating from the same source have their transverse vibrations at each instant parallel to one another, so that they are in the right condition for interference.

The preceding experiments show then that the vibrations of the ether are parallel to the wave-surface, and that in a polarised ray they take place, for the most part, in one plane passing through the ray. Moreover, *the vibratory movements are perpendicular to the plane of polarisation*. For when a beam of light passes through a crystal with one optic axis, like Iceland spar, the *ordinary* ray is polarised in a plane parallel to the principal section of the crystal; that is to say, it is most easily reflected in a plane parallel to that section (p. 653). Now as this ray follows the ordinary law of refraction, and consequently has a constant velocity whatever direction it may take through the crystal, the vibrations of the ether which form it must have a constant direction with regard to the axis of the crystal; and as they are perpendicular to the ray whatever angle it may make with the axis, they could not form a constant angle with the axis, unless they were also perpendicular to that axis. The vibratory movements constituting the ordinary ray are therefore perpendicular, both to the ray and to the optic axis, and therefore to the principal section, which is the plane passing through the ray and the axis, and in this case is identical with the plane of polarisation of the ray. Hence, as all polarised rays possess the same properties, whatever may be their origin, it follows that the vibrations of the ether are always at right angles to the plane of polarisation.

The same result may be deduced from the properties of the tourmaline, which, as already observed (p. 655), intercepts the ordinary ray. Now it is found that a plate of tourmaline, cut *perpendicular to the optic axis*, intercepts all the light which falls upon it at perpendicular incidence, which shows that all vibrations perpendicular to the axis are arrested by it. But when the ray passes through a plate of tourmaline cut parallel to the axis, only the ordinary ray is intercepted, the extraordinary ray passing through. The vibrations of the ordinary ray must therefore be perpendicular to the axis, and consequently to the principal section of the crystal, parallel to which the ray is polarised.

From this direction of the vibratory movements, it follows that a polarised ray is most easily reflected when its vibrations are parallel to the reflecting surface, and on the contrary, that it is most easily transmitted through a pile of plates when the vibrations take place in the plane of incidence or at right angles to the surface; also that the ray passes most completely through a tourmaline cut parallel to its axis, when the vibrations are parallel to this axis. The tourmaline acts therefore like a grating, which gives free passage to a surface, such as a knife-blade, parallel to the bars, but stops it when presented transversely.

Fig. 677.



The form of the curve which the ether-molecules describe in the plane perpendicular to the direction of the ray—for example, in the row *a a'* (*fig.* 677)—determines the state of polarisation of the ray. If the oscillation consists in a mere motion of the particles backwards and forwards in a straight line, the ray is said to be rectilinearly polarised, or plane-polarised; and the plane passing through the ray at right angles to the direction in which the particles vibrate, is the plane of polarisation of the ray. The particles originally situated in the straight line which is the direction of the ray, appear at a certain moment, arranged in the wave-line *acb*. If each of the vibrating particles describes a circle, the direction of its velocity will change from 0° to 180° while the vibration is extending through the space of half an undulation, and to 360° in the space of a whole undulation: hence, a series of particles in all phases of velocity, extending from one extremity of the wave to the other, will be situated on a screw-line having the direction of the ray for its axis. The ray is then circularly polarised, and right or left, according as the direction of revolution of the ether-molecules, regarded from the centre of the circle, or the axis of the screw, is like that of the hands of a watch or the contrary. The result is the same as if the ray were polarised in one plane, and this plane revolved, making a complete revolution during the time of one vibration.

If each of the vibrating particles describes an ellipse, the successive particles may be conceived as arranged on an elliptical screw-line. In this case, to determine the state of polarisation of the ray, it is necessary to specify, not only the length of the major and minor axes of the ellipse, but likewise the position of these axes in space, as determined, for example, by a system of rectangular co-ordinates, one axis coinciding with the ray, while the other two are drawn at right angles to each other in the plane of vibration of the ether-molecules. The direction of the rotation must also be stated as in the case of circular polarisation.

A circularly polarised ray examined by an analyser exhibits the same intensity in all azimuths, just like natural light, but is distinguished therefrom by appearing coloured when viewed through the analyser, after passing through a thin plate of a double refracting crystal (p. 671). An elliptically polarised ray exhibits a maximum and minimum of intensity in two positions of the analyser at right angles to each other, but is never completely extinguished like a plane-polarised ray, and is likewise coloured by transmission through a double-refracting film. The colours thus imparted both to circularly and to elliptically polarised light, differ from those exhibited under similar circumstances by plane-polarised light.

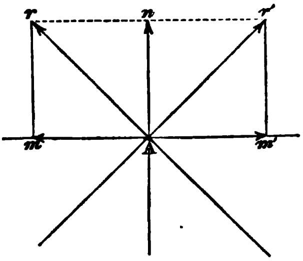
To understand the manner in which these different states of polarisation arise, it is necessary to take account of the movement impressed upon the molecules of the ether when they transmit several systems of waves at once, the velocities being then compounded according to the principle of the parallelogram of forces. When this composition is effected by construction or by calculation, it is found that when the lengths of the component waves are equal (the only case that will be here considered) the waves of the resulting system always have the same length, so that the changes produced can affect only the amplitude of vibration and the state of polarisation.

1. *When the two rays are polarised in the same plane.*—In this case, the amplitude of the resultant wave is equal to the sum or difference of the component waves, according as the two rays are in corresponding or in opposite phases; and if they are in exactly opposite phases, and of equal amplitude, they destroy each other's motion

completely, and produce darkness. The case is, in fact, that already considered under INTERFERENCE (p. 598).

2. *When the two rays are polarised at right angles to each other.*—In this case, the vibrations of the two wave-systems take place in planes at right angles to one another, and therefore the resulting system cannot be rectilinearly polarised, unless the difference of phase of the two component wave-systems is either nothing or an exact multiple of a half wave-length. If we imagine two rays travelling at right angles to the surface of the paper, and passing through the point A (*fig.* 678), the vibrations of the first (positive) half-wave of the one system being directed parallel to A*n*, and those of the other parallel to A*m*; then if both the waves affect the particle A simultaneously and with equal force, the resulting vibrations will make an angle of 45° with those of the component wave. The azimuth of the vibration is then 45°, reckoning from A*n*. If, on the other hand, the second system is half a wave-length before or behind the other, it will affect the particle A with its negative vibration A*m'*, at the same time that the positive vibration A*n* of the other system begins to act. The azimuth of vibration is then −45°, always reckoning from A*n*.

Fig. 678.



But if the difference of phase of the two wave-systems is equal to a quarter of a wave-length, the velocity A*m* then affects the particle A, just as the vibration imparted to it by the other system has brought it to *n*, and it is about to return towards A: it therefore acquires a rotatory movement round the point A. The ray is therefore circularly polarised, and right or left, according as the system A*m* is before or behind the system A*n* by a quarter of an undulation. If the amplitudes of the two systems are unequal, a difference of phase amounting to a quarter of a wave-length will produce elliptical polarisation. This kind of polarisation is likewise produced with any other difference of phase $\left(\text{excepting } 0 \text{ or } m \,.\, \frac{\lambda}{2}\right)$, whether the amplitudes are equal or unequal.

If the two systems are polarised in planes making an oblique angle with one another, a difference of phase equal to 0 or $m \,.\, \frac{\lambda}{2}$ produces rectilinear or plane polarisation, while every other difference produces elliptical polarisation.

It follows, from the preceding considerations, that elliptical polarisation is the usual state of polarised light, circular and rectilinear polarisation being merely particular cases of it.

Suppose now a plane-polarised ray to fall on the separating surface of two transparent media, its plane of vibration being inclined to the plane of incidence at an angle of 45°. Each vibration may then be regarded as resolved into a component (*P*) vibrating in the plane of incidence, and another (*R*) vibrating at right angles to that plane; and these two components will be weakened by reflection in unequal degrees. At the incidences 90° and 0° (measured from the normal), the two components of the reflected ray are of equal intensity; but from 90° to 0° the intensity of *R* continually diminishes, whereas that of *P*, though it likewise diminishes for a certain distance from 90° towards 0°, attains a minimum value at a certain angle of incidence, whose magnitude depends on the refractive index, and increases again from that point up to perpendicular incidence.

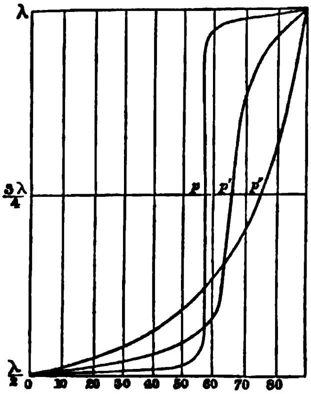
In reflection from metals, and also from non-metallic substances of high refractive power, the quotient $\frac{P}{R}$ has always a considerable value; but in the case of media of comparatively low refractive power, such as water and glass, it very nearly vanishes at the limiting angle above mentioned. Moreover, as the variously directed vibrations of an ordinary (unpolarised) ray may be resolved into the two principal components above mentioned, it follows that, at the limiting angle, the vibrations of the ray (if monochromatic) will all, or nearly all, be reduced to one plane—namely, a plane perpendicular to the plane of incidence; in other words, the ray, after reflection, will be completely polarised, or nearly so, in the plane of incidence. The limiting angle above referred to is therefore the polarising angle (p. 653). It is clear also that if the ray thus polarised falls upon a second mirror at the same angle, and this mirror is so placed that the vibrations of the polarised ray are parallel to its plane of incidence, little or no light will be reflected from it; but that, if the second reflector be turned round from this azimuth, always remaining at the same angle to the ray, the quantity of light reflected will gradually increase till the plane of incidence upon the second mirror coincides with that upon the first, at which the quantity of light reflected from the second mirror will be a maximum. (See page 653.)

When light falls at the polarising angle on a substance of comparatively small refracting power, as glass, water, &c., the intensity of the refracted ray is much greater than that of the reflected ray, inasmuch as a small portion of the light polarised at right angles to the plane of incidence, and nearly the whole of that which is polarised parallel to the plane of incidence, pass into the refracted ray. The former component unites with an equal portion of the latter, reproducing unpolarised light, so that the refracted ray consists of natural light mixed with light polarised in the plane of incidence.

The two components P and R not only differ in intensity after reflection, but likewise exhibit a difference of phase, P being always more or less behind R, excepting, according to Jamin, in reflection from one or two varieties of silica.

At the incidence of 90°, since a ray polarised in the azimuth of 45° retains its azimuth unaltered, the difference of phase of the two components P and R is either nothing or equal to an entire wave-length (p. 659). At perpendicular incidence, the azimuth changes from 45° to $-45°$; consequently the difference of phase is $\frac{\lambda}{2}$. In both cases, therefore, a plane-polarised ray remains plane-polarised after reflection. But at all other incidences, the difference of phase is between λ and $\frac{\lambda}{2}$, and consequently the plane or rectilinear polarisation is converted into elliptical polarisation. The angle of incidence for which the difference of phase $= \frac{3\lambda}{4}$ is called the **principal incidence**. It is very little smaller than the polarising angle (p. 653), calculated from Brewster's formula, $\tan i = \mu$: hence, at the principal incidence, the quotient $\frac{P}{R}$ differs but little from its smallest value. In substances of small refracting power, the passage from the difference of phase $\frac{\lambda}{2}$ to λ takes place quickly, so that the elliptical polarisation is perceptible only between very narrow limits; but in bodies of greater refracting power, such as diamond, it is more easily observed. *Fig.* 679, in which the angles of incidence are laid down as abscissæ, and the differences of phase diminished by $\frac{\lambda}{2}$ as ordinates, exhibits the difference of behaviour of glass, sulphide of arsenic, and zinc. The points p, p', p'' correspond to the principal incidences, or to a difference of phase $= \frac{3\lambda}{4}$.

Fig. 679.



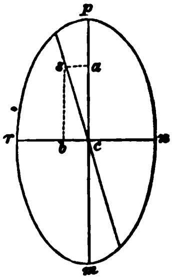
The more refrangible rays acquire a greater difference of phase in their two components under a given incidence than the less refrangible rays. In many metals, as silver, copper, brass, and nickel-silver, the ratio of the intensities $P : R$ is smaller, while in others, as zinc and steel, it is larger for the more refrangible rays. In consequence of this inequality, the former metals, especially when illuminated by light vibrating in the plane of reflection, exhibit a yellow or red, the latter a bluish colour, the tints often coming out with continually greater distinctness after repeated reflection. At the incidence of 90°, that is to say, when the incident ray just grazes the surface, all well-polished metals appear white.

Theory of Double Refraction.

The phenomena of reflection, refraction, and coloration undergo considerable alterations when light falls upon media through which it travels with different velocities in different directions. This is the case in all crystals not belonging to the regular or monometric system; likewise in all media whose molecular condition is altered in particular directions by pressure, or by heating and sudden cooling, such as unannealed glass.

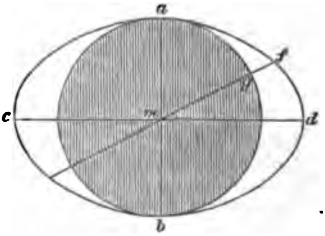
Crystals with one Optic Axis.—Consider, in the first place, crystals belonging to the dimetric and hexagonal systems, which resemble one another greatly in their optical as well as in their other physical properties, such as expansion by heat (iii. 72), and capacity of conducting heat and electricity (ii. 122). In these crystals, the elasticity of the ether is either greatest (negative crystals), or least (positive crystals), in the direction of the principal crystallographic axis, but equal in all directions at right angles to that axis. If, now, from any point within the crystal, straight lines be drawn in all directions, and proportional in length to the square roots of the elasticities of the ether in these several directions, the terminal points of these lines will be situated on a surface of revolution called the surface of elasticity. To find the velocities with which rays are transmitted in these several directions, imagine a number of plane waves to pass in all directions through the centre. Every such wave cuts the surface of elasticity in a closed curve, like *fig.* 680. If the crystal is negative—calcspar, for example—the longest diameter of this curve lies in a meridional plane (called, in optical language, the principal section), the shortest diameter in the equatorial plane of the surface of elasticity. If the light-wave is polarised, and its vibrations take place in the direction *cs*, it will, after penetrating through an extremely thin layer of the crystal, divide itself into two polarised waves, which vibrate in the directions of greatest and least elasticity, *cp* and *cr*, with the amplitudes *ca* and *cb*, and will therefore travel with unequal velocities in the direction perpendicular to *mnpr*. It is as if the molecules of the ether were compressed in the direction of the principal axis, so that a vibratory movement cannot easily be propagated in a direction oblique to that axis, but is resolved into two in the manner above mentioned.

Fig. 680.



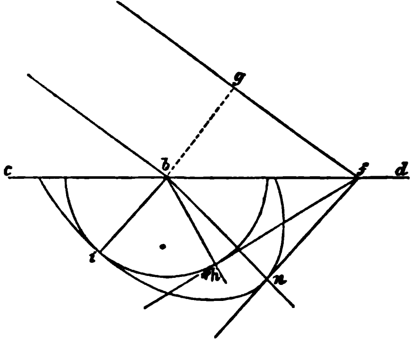
The same result will ensue if the incident wave consists, not of polarised but of natural light, excepting that the two polarised components will then have equal intensities, since they are made up, not only of the components of vibrations in the direction *cs*, but likewise of those of vibrations in all other directions within the plane *mnpr*. If the incident wave coincides with the equatorial plane of the surface of elasticity, the two semidiameters *cp*, *cr* are equal. In this case, the light is not polarised in two directions at right angles to one another, but the wave travels onwards without dividing itself, in the direction of the principal crystallographic axis, which, on account of this property, is denominated the optic axis. Crystals of the dimetric and hexagonal systems are optically uniaxial.—If the plane wave passing through *c* coincides with a meridional plane, the difference of the two velocities of transmission is a maximum, since one of the components calls into action the maximum amount of elasticity in the direction of the axis itself. The velocity of transmission of the other component remains, as above mentioned, the same in all directions, inasmuch as it is always proportional to the radius, *cr*, of the surface of elasticity. If, now, we imagine the infinite number of plane wave-surfaces passing in all directions through the point *c* set in motion at the same time, according to the laws above detailed, they will, after a short time, enclose two different curved surfaces called the wave-surfaces of monoaxial crystals. One of these surfaces, corresponding to the light which vibrates in the equatorial plane, or at right angles to the principal section (*i.e.* polarised in the principal section, p. 657), is a sphere; the second, corresponding to that which vibrates in the principal section (or is polarised at right angles to that section), is shown by calculation to be an ellipsoïd of revolution, which touches the sphere at two points situated on the optic axis. *Fig.* 681 is a meridional section of the two wave-surfaces. In any direction through such a crystal, two rays, polarised at right angles to each other, travel with the velocities *mg* and *mf*. The vibrations of the first ray are perpendicular to its direction, but those of the second are not; they take place in a plane touching the ellipsoïd at the point *f*, so that, to find the velocity of transmission of the plane wave corresponding to the ray *mf*, it is necessary to draw a perpendicular from *m* to the plane which touches the ellipsoïd *mf*.

Fig. 681.



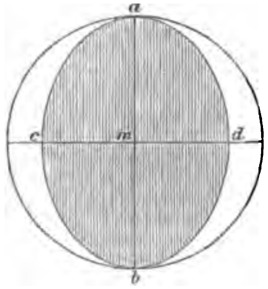
From this theory, first developed by Fresnel, all the phenomena of double refraction may be deduced in a very simple manner. Suppose a beam of parallel rays corresponding to the plane wave *bg* (*fig.* 682) to fall upon the surface of a monoaxial crystal—calcspar, for example—whose optic axis is in the direction *bi*. Round *b* as a centre describe the two wave-surfaces, so that, taking *gf* as unity, the radius of the spherical surface may be $\frac{1}{3{\cdot}654}$, and that of the ellipsoïd $\frac{1}{1{\cdot}483}$. Imagine also a line drawn through f at right angles to the plane of the figure, and through this line suppose planes to pass touching the sphere in h, the ellipsoïd in n; then, as explained with reference to *fig.* 655 (p. 609), $b\,h$ and $b\,n$ will be the directions of the two refracted rays. The vibrations of the ray bh are perpendicular to the plane of incidence, which in this case is also the principal section; those of the ray $b\,n$ are parallel to the plane of incidence. The ratio of the velocities of the ray $b\,h$, without and within the crystal, is independent of the angle of incidence, as in uncrystallised media and crystals belonging to the regular system (isophanous media), since the corresponding wave-surface is a sphere. This ray is therefore called the ordinary ray (O). But the index of refraction of the second ray, bn, varies with the angle of incidence: hence this ray is called the extraordinary ray (E). In calcspar, and all other negative crystals, it is less than that of the ordinary ray.

Fig. 682.



If the plane of incidence neither coincides with a principal section, as in the preceding example, nor is perpendicular thereto, the plane drawn through f tangential to the ellipse will touch it in a point not contained in the plane of incidence; the extraordinary ray then deviates from the plane of incidence, which is never the case in ordinary refraction. As in negative crystals, the extraordinary ray is always less refracted than the ordinary ray, and, in comparison with this, appears to be repelled from the optic axis, these crystals are sometimes called repulsive: positive crystals, on the other hand, in which the extraordinary ray is more refracted than the ordinary ray, are called attractive crystals.

Fig. 683.



The optical relations of positive uniaxial crystals are exactly similar to those of negative crystals, excepting that, as the elasticity of the ether is a minimum in the direction of the optic axis, the velocity of the light in this direction is a maximum. The wave-surface of the ordinary ray encloses that of the extraordinary ray, as shown in section in *fig.* 683. The ray E in these crystals—rock-crystal, for example—is more strongly refracted than O.

The following is a list of the most important uniaxial crystals:

Positive or Attractive Crystals.

Zircon.
Quartz.
Tungstate of zinc.
Stannite.
Boracite.
Apophyllite.
Sulphate of potassium and iron.
Acid acetate of copper and calcium.
Hydrate of magnesium.
Ice.
Hyposulphate of calcium.
Dioptase.
Red silver.

Negative or Repulsive Crystals.

Iceland spar.
Carbonate of calcium and magnesium.
Carbonate of calcium and iron.
Tourmaline.
Rubellite.
Corundum.
Sapphire.
Ruby.
Beryl.
Apatite.
Idocrase.
Wernerite.
Mica.
Phosphate of lead.
Arsenio-phosphate of lead.
Hydrate of strontium.
Arsenate of potassium.
Chloride of calcium.
Chloride of strontium.
Basic phosphate of potassium.
Sulphate of nickel and copper.
Cinnabar.
Mellite.
Molybdate of lead.
Octahedrite.
Phosphate of calcium.
Arsenate of lead.
Arsenate of copper.
Nepheline.

From the explanation just given of double refraction in uniaxial crystals, it follows that, for the complete optical characterisation of such a body, it is sufficient to know the greatest and least velocities of light therein, or—which comes to the same thing—the indices of refraction for the two oppositely polarised rays which traverse the crystal in a plane perpendicular to the axis. To find these indices of refraction, the crystal must be cut in the form of a prism, with its refracting angle parallel to the optic (or principal crystallographic) axis, and the least deviations of the several coloured rays in the ordinary and extraordinary image measured by the methods already described. The values thus found are, of course, true only for the particular temperatures at which they are measured. Change of temperature likewise affects the refractive indices of double-refracting crystals in a peculiar manner, because the rate of expansion by heat of these crystals, in the direction of the optic axis, is not the same as in directions perpendicular to that axis. Calcspar, for example, expands in the direction of its optic axis joining two obtuse summits of the rhombohedron, more strongly than in any other direction, the rhombohedron at the same time approaching in form to the cube, while the double refraction perceptibly diminishes, or, in other words, the refractive indices of the rays *E* and *O* approach more nearly to equality. Very exact measurements of indices of refraction of Fraunhofer's seven lines (*B*—*H*), in the ordinary and extraordinary images of calcspar and rock-crystal, together with the alterations produced in them by change of temperature, have been made by Rudberg (Pogg. Ann. xiv. 45; xxvi. 291). Double refraction is frequently also different in degree for the different coloured rays. In apophyllite, indeed, this inequality is so great that the crystal is positively double-refracting for the blue, negatively for the red rays, and single-refracting for an intermediate ray.

2. *Crystals with two Optic axes.*—In all crystals belonging to the remaining systems, viz., the trimetric, monoclinic, diclinic, and triclinic, there are two directions or axes in which an ordinary ray of light may pass without being split into two. Hence these crystals are called bi- or di-axial. The somewhat more complex phenomena which they exhibit are also completely explained by Fresnel's theory.

The elasticity of the ether in these crystals is of unequal magnitude in three directions at right angles to each other (the three axes of elasticity). If we call the modulus of greatest elasticity a^2, of the middle b^2, and of the least c^2, and imagine lines drawn from the centre of the crystal in all directions, proportional to the square roots of the elasticities called into activity in these several directions, the ends of these lines will be situated on a surface, called the surface of elasticity, having three unequal axes, $2a$, $2b$, $2c$, at right angles to one another; and if plane waves be supposed to pass through the centre of this surface in all possible directions, as in the case of uniaxial crystals, each of these will cut the surface of elasticity in a closed curve. All vibrations in such a plane wave-surface are very quickly resolved in the direction of the greatest and least diameters of the plane section, which are perpendicular to one another; and the wave is divided into two which travel onwards parallel to each other, but with unequal velocities, proportional to the square roots of the elasticities which are set in action in the direction of those diameters. If all these plane waves are supposed to be set in motion at once, they will, after a given time, enclose the wave-surface of biaxial media.

Fig. 684 exhibits three sections of the wave-surface cutting one another at right angles. Of the two perpendicular to the plane of the figure, the vertical section contains an ellipse enveloped by a circle; the horizontal section, a circle enveloped by an ellipse; the section in the plane of the paper consists of an ellipse and a circle intersecting one another: they are represented separately in *fig.* 685. The circle in each section belongs to rays whose vibrations are perpendicular to the plane of that section, and therefore in the direction of an axis of elasticity: such rays suffer ordinary refraction. The ellipse, on the other hand, gives the velocity of transmission of the extraordinary rays, whose vibrations are parallel to the plane of the section. To obtain the three characteristic refractive indices of μ, μ', μ'' of a biaxial crystal, three prisms must be cut, having their refracting angles respectively parallel to the three axes of elasticity, and the minimum deviation of the seven principal rays determined in each of them, for that one of the two coloured images, whose plane of polarisation is perpendicular to the refracting angle. This measurement has been very carefully performed by Rudberg for arragonite and topaz. Both the refractive indices, and the ratios between them, vary with the temperature in biaxial as well as in uniaxial crystals.

The ratios $\frac{\mu''}{\mu}$, $\frac{\mu''}{\mu'}$, which express the strength of the double refraction, appear to increase in all crystals from the less to the more refrangible rays. In crystals of the trimetric system, the axes of elasticity have the same direction for all the coloured rays. The crystals of the mono-, di-, and tri-clinic systems appear to exhibit a different behaviour in this respect. Their peculiarities will be considered in connection with the colours which they exhibit in polarised light (p. 669).

Fig. 684.

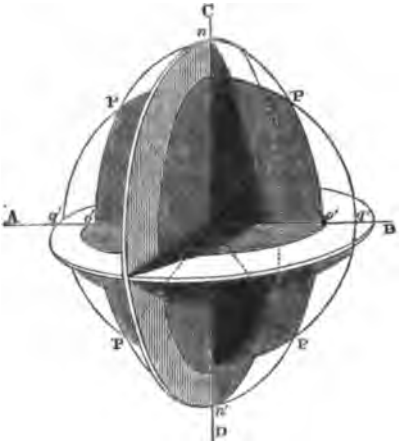
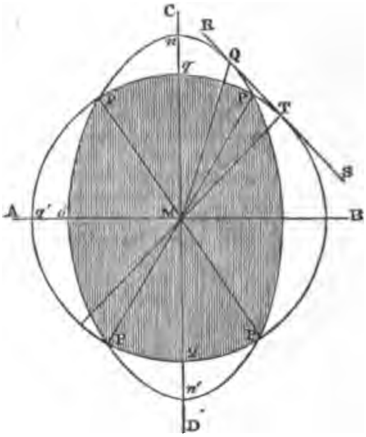
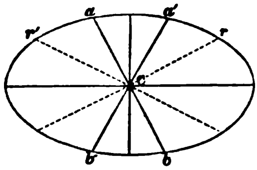


Fig. 685.





In two directions, *ab* and *a'b'* (*fig.* 686) making equal angles with the axis of greatest, and also with that of least elasticity, the surface of elasticity is cut in circles. At right angles to the planes of these circles, and therefore in the directions *Cr*, *Cr'*, a plane wave is propagated without being resolved into others, or altered as to its state of polarisation. These directions were designated by Fresnel, as the true optic axes of the crystal. But, as shown by *fig.* 685, there are likewise two directions in which the ordinary and extraordinary rays, which, therefore, belong to different waves, are transmitted with the same velocity. These directions, which unite the points of intersection P of the ellipse and circle with the centre M, have received the name of apparent optic axes.

As may be seen from the figure, it depends upon the ratio of the mean velocity of transmission M*q* to the greatest M*n* and least M*o'*, whether the apparent optic axes form a smaller angle with the axis of greatest elasticity and least velocity of transmission, or with that of least elasticity and greatest velocity of transmission. In the former case, the crystal approximates in its optical character to calcspar, and is therefore called optically negative (*e.g.* arragonite); in the latter, to rock-crystal, and is therefore called optically positive (*e.g.* topaz). The line which bisects the acute angle of the optic axes is the median line; that which bisects their obtuse angle, the supplemental line; and the line perpendicular to both of these is the normal. The last is always the axis of mean elasticity; the median line coincides with the axis of greatest elasticity in negative, and with that of least elasticity in positive crystals.

To find the rays belonging to a given plane wave-surface, planes must be drawn parallel to this plane and tangential to the wave-surface, and the points of contact joined with the centre. This construction always yields two tangent-planes, and therefore two rays. It is only when the wave-plane is perpendicular to one of the true optic axes, that the two tangent planes coincide in one, which, however, then touches the wave-surface in a circle. At the point P (*fig.* 685), the wave-surface forms funnel-shaped depressions or re-entering cones, the plane wave RS, which is perpendicular to the true optic axis MT, closing the funnel and touching the curved wave-surface in a circle having the diameter QT. To this wave-plane, therefore, correspond all rays proceeding from the centre M to the several points of the circumference of that circle. If, therefore, a ray of common light falls upon a plate of arragonite cut and polished at right angles to the median line, in such a direction that it would emerge in the direction of the true optic axis, it divides itself into a conical beam of rays, which, as they belong to the same wave-plane, proceed, after emerging, parallel to one another in a cylindrical beam. This phenomenon, the so-called cylindrical or inner conical refraction, becomes perceptible only when the arragonite plate has a thickness of at least a centimetre.

Every line drawn from the centre to the surface of the wave, *e.g.* MT or MQ, cuts this surface in two points corresponding to the two rays which travel in this direction. The wave-planes belonging to these rays are found by drawing tangent-planes to the points of intersection with the upper wave-surface. It is only the ray MP, which travels in the direction of the apparent optic axis, that cuts the wave-surface in a single point only: at this point, however, the wave-surface has an infinite number of tangent planes; and, consequently, since the velocity of the wave-plane within the crystal determines the strength of the refraction, the ray MP yields an infinite number of refracted rays diverging from one another in a cone. This remarkable phenomenon, called external conical refraction, may be observed by covering the two parallel faces of a plate of arragonite cut perpendicular to the median line, with screens, each having a fine aperture so situated that the line joining the two apertures coincides with an apparent optic axis of the crystal. If a converging pencil of rays from a near source of light be directed on one face of the arragonite plate, a conically divergent pencil emerges from the other.

The polarisation phenomena of the two rays proceeding in any given direction are easily determined. If planes be made to pass through the ray and the two apparent optic axes, the direction of vibration of the one ray bisects the acute, and that of the other ray the obtuse angle of the two planes. The directions of vibration (and therefore also the planes of polarisation) of the two rays are therefore always perpendicular to one another.

If the three characteristic refractive indices, μ, μ', μ'', of a crystal are known, and $\mu'' > \mu' > \mu$, then, as Fresnel has shown, the angle 2β of the true optic axes may be calculated by the formulæ:

For negative crystals. For positive crystals.

$$\sin^2\beta = \frac{\mu^2}{\mu'^2} \cdot \frac{\mu''^2 - \mu'^2}{\mu''^2 - \mu^2}; \qquad \sin^2\beta = \frac{\mu''^2}{\mu'^2} \cdot \frac{\mu'^2 - \mu^2}{\mu''^2 - \mu^2};$$

and the angle 2α of the apparent optic axes by the formulæ:

$$\sin^2\alpha = \frac{\mu''^2 - \mu'^2}{\mu''^2 - \mu^2}; \qquad \sin^2\alpha = \frac{\mu'^2 - \mu^2}{\mu''^2 - \mu^2}.$$

It will be seen that, in negative crystals, the apparent optic axes form a somewhat larger angle than the true optic axes, whereas in positive crystals the contrary is the case.

TABLE OF BIAXIAL CRYSTALS.

	Angle of axes.
Sulphate of nickel (certain specimens)	3° 0′
Nitrate of potassium	5 20
Carbonate of strontium	6 56
Carbonate of barium	6 56
Talc	7 24
Sulphocarbonate of lead	10 35
Mother of pearl	11 28
Hydrate of barium	13 18
Arragonite	18 18
Cyanide of potassium	19 24
Cymophane	27 51
Anhydrite	28 7
Borax	28 42
Apophyllite	35 8
Sulphate of magnesium	37 24
Sulphate of barium	37 42
Spermaceti (about)	37 40
Borax (native)	38 48
Nitrate of zinc	40 48
Stilbite	41 42
Sulphate of nickel	42 4
Anhydrite (Biot)	44 41
Lepidolite	45 41
Benzoate of ammonium	45 8
Sulphate of sodium and magnesium	46 49
Sulphate of ammonium	45 8
Topaz	49° to 65 0

	Angle of axes.
Sugar	50° 0′
Sulphate of strontium	50 0
Sulphohydrochlorate of magnesium and iron	51 16
Sulphate of magnesium and ammonium	51 22
Phosphate of sodium	55 20
Comptonite	56 6
Sulphate of calcium	60 0
Nitrate of silver	62 16
Iolite	62 50
Felspar	63 0
Sulphate of potassium	67 0
Carbonate of sodium	70 1
Acetate of lead	70 25
Citric acid	70 29
Tartrate of potassium	71 20
Tartaric acid	79 0
Tartrate of potassium and sodium	80 0
Carbonate of potassium	80 30
Cyanite	81 48
Chlorate of potassium	82 0
Epidote	84 19
Chloride of copper	84 30
Peridote	87 56
Succinic acid (about)	90 0
Sulphate of iron (about)	90 0
Mica	0° to 76 0

It will be observed that topaz, and more especially mica, exhibit very different angles in different specimens. Sénarmont explains this anomaly by regarding these bodies as mixtures of two isomorphous substances, in which the planes of the axes are perpendicular to each other. He has shown, in fact, that a crystal formed by a mixture of two substances has its axes more or less inclined to one another, or situated in planes whose position varies by 90° from one specimen to another, according to the proportions of the mixture. In the case of mica, which, as Sénarmont has shown, crystallises in right prisms with rhombic base (trimetric), the plane of the axes is parallel, sometimes to the longer, sometimes to the shorter diagonal of the base. (Daguin, *Traité de Physique*, iv. 489.)

Reflection of Light from Double-refracting Media.—The reflection of light from the surface of double-refracting crystals follows, so far as regards the difference of phase of the two principal components polarised parallel and perpendicular to the plane of incidence, the same laws as those which are observed in reflection from isophanous media.

On the other hand, the alterations in the azimuth of polarisation depend, not only on the angle of incidence, but likewise on the inclination of the reflecting surface, and the plane of incidence to the axes of the crystal. Even when a polarised ray falls perpendicularly on a double-refracting surface, the azimuth of polarisation does not remain unaltered. In particular cases, however, no alteration takes place: for example, in uniaxial crystals, when the reflecting surface is perpendicular to the optic axis, or when the plane of incidence coincides with the principal section. For each relative position of the reflecting surface and the plane of incidence, there is always an angle of incidence at which the azimuth remains unaltered. It must also be observed, that when light is reflected within a double-refracting medium, each incident ray gives two reflected rays; that in uniaxial crystals, only one of the reflected rays remains constantly in the plane of incidence, whereas the other may deviate therefrom; and that in biaxial crystals, for the most part, neither of the two reflected rays remains in the plane of incidence.

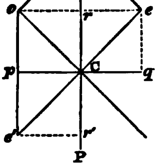
Colours of Polarised Light.

Double-refracting substances viewed in polarised light often exhibit brilliant colours, the exact observation of which affords, in most cases, an easier method of determining the position of the axes of the crystal, than the mere separation of a ray of light into two, which is distinctly perceptible only when the double refraction is strong, and the crystal has a considerable thickness. Hence, the observation of these coloured phenomena is of great service in the study of crystalline structure.

Since the two rays into which an incident ray of common light is divided on entering a double-refracting medium travel through that medium with unequal velocities (p. 661), they will, on emerging from the medium, exhibit a certain difference of phase. As, however, the vibrations of the two rays always take place in planes at right angles to one another, they cannot interfere so as to produce any coloration or variation of intensity. Hence, the two images seen through a double-refracting crystal in ordinary light are colourless.

But the case is different when the crystalline plate is viewed in a polarising apparatus, say, between two tourmalines, or two Nichol's prisms, one serving as polariser, the other as analyser (p. 655). The rays which fall on this plate are then polarised by the action of the first prism or tourmaline, that is to say, their vibrations are reduced to one plane. If this plane is parallel to one of the directions of vibration in the double-refracting plate, they pass through it without further decomposition, so that only one ray—ordinary or extraordinary, as the case may be—passes through the plate. But if the direction of vibration CP (*fig.* 687) of the polariser is inclined at 45° to the two directions of vibration C*o*, C*e*, of the double-refracting plate, two components, C*o*, C*e*, of equal intensity are obtained. Suppose now that the difference of path of the two corresponding rays, after passing through the plate, is equal to an even number of half wave-lengths; the vibrations will then proceed simultaneously from C towards *o* and *e*; and if the direction of vibration, *pq*, of the analyser is at right angles to that of the polariser, P*s*, the vibrations C*o*, C*e*, will then yield two equal and opposite components, C*p*, C*q*, which will destroy one another. Consequently, if the incident light is monochromatic, the field of view, in this position of the analyser, will be dark. If, on the other hand, the polariser and analyser are placed with their axes parallel, so that *pq* coincides with CP, the components of C*o* and C*e* will both lie in the direction C*r*, and will strengthen one another, so that the field will be light.

Fig. 687.



If the difference of path of the ordinary and extraordinary rays is equal to an uneven number of half wave-lengths, the vibrations will proceed from C simultaneously in the directions *Co* and *Ce′*; consequently, the phenomena just described will be exactly reversed, the field being dark when the axes of the two tourmalines or Nichol's prisms are parallel, and light when they are crossed.

When the incident light is white, it is only particular coloured rays that destroy each other completely, or strengthen one another's effect in the greatest degree; consequently, the field is never dark, but the double-refracting plate appears coloured, the colours varying according to the thickness of the plate; and for any particular thickness, being complementary to one another in the two relative positions of the polariser and analyser. When a double-refracting prism (p. 655) is used as analyser, two images are seen, the colours of which are complementary to one another; and if they are large enough to intersect, the overlapping portion is white.

When a thin wedge-shaped plate of a double-refracting crystal—gypsum, for example—is placed between the crossed Nichol's prisms or tourmalines, a series of coloured stripes is observed following exactly the order of colours of Newton's rings (p. 646). In the thinnest part, the wedge is colourless, because there the difference of path of *o* and *e* is only a small fraction of the wave-lengths of all the coloured rays. At a somewhat greater thickness, the violet and blue rays disappear first, and the colour passes through yellowish white and orange into red of the first order. Beyond this point the yellow and red rays disappear, and a blue stripe is produced, and so on. When the thickness is so great that the difference in length of path of *o* and *e* amounts to a multiple of the wave-lengths of a great number of rays diffused through the entire spectrum, the remaining rays together produce white light: hence plates of double-refracting substances, above a certain thickness, no longer appear coloured in polarised light. If, however, the white light which has passed through such a plate be decomposed by a prism, the resulting spectrum is seen to be traversed by a great number of black lines.

When the tourmalines or Nichol's prisms are placed with their axes parallel, the colours produced are complementary to those above described; hence it is clear that unpolarised light can never produce any colours in double-refracting plates, inasmuch as it consists of vibrations in all possible azimuths, so that the colour produced by any particular set of vibrations is exactly compensated by the complementary colour of another set at right angles to the first, the two together reproducing white light.

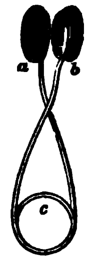
A thin film of gypsum in which a circular cavity of very long radius is made, exhibits in polarised right a series of coloured rings exactly similar to Newton's rings.

The order of the colour of any crystalline plate in polarised light may be determined by laying it over the above-described wedge, in such a manner that the *o* of the plate may coincide in its direction of vibration with the *e* of the wedge. At the place where the plate and wedge give equal differences of path, their actions compensate one another, so that a black stripe is seen with the tourmalines crossed, and a white stripe if they are parallel. The order of the colour may then be read off on the wedge.

We have hitherto supposed the plate to be placed at right angles to the rays. On gradually inclining it, the colours change—first, because the rays have then to pass through a greater thickness of the plate; secondly, because the angle which the rays form with the axis or axes of the crystal also varies, and this circumstance likewise affects the difference of path corresponding to a given thickness of the crystal.

Coloured Rings.—A plate of a double-refracting crystal cut perpendicularly to the axis does not exhibit the colours above described when viewed by parallel rays, because, in the direction of the axis, the two rays *o* and *e* have equal velocities, or, in other words, are reduced to one ray. But, when diverging light, proceeding from a luminous point at a short distance, is made to pass through the crystalline plate placed between two tourmalines, or when the analysing tourmaline is placed so close to the eye that the visual rays converge strongly towards the optic centre of the eye, brilliantly-coloured rings are produced, the form of which differs according as the crystalline plate is uniaxial or biaxial.

Fig. 688.



A simple apparatus for viewing these phenomena consists of two plates of tourmaline capable of rotating in their own planes in two rings, or sockets, *a*, *b* (*fig.* 688), fixed to the end of a spring, *c*, so that the crystalline plate, attached to a piece of cork, may be firmly held between them, but still be capable of turning round in its own plane.

A plate of a uniaxial crystal, such as calcspar, cut with parallel faces perpendicular to the optic axis, exhibits, when viewed between the crossed tourmalines, a series of circular coloured rings, intersected by a black cross (*fig.* 689). If, on the other hand, the tourmalines are placed with their axes parallel, the cross is white, as in *fig.* 690, and the colours are complementary to the former. To understand their formation, it is merely necessary to remember that, in the direction of the axis *ba* (*fig.* 690), the rays *o* and *e* have equal velocities, but that their difference of path becomes greater and greater in proportion as they are more inclined to the axis because, in the first place, the difference of velocity of the two rays then becomes continually greater; and, secondly, because the thickness of the plate which has to be traversed by the rays increases at the same time. The colours which, in the wedge above described (p. 667), are arranged parallel to the edge are, in this case, grouped in concentric circles round the axis, the order of the tints being again that of Newton's rings.

Fig. 689.

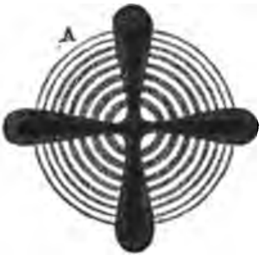
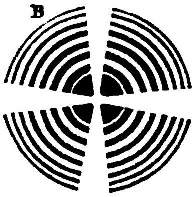


Fig. 690.



The vibrations parallel and perpendicular to the axis of the second tourmaline not being resolved into two components, there can be no interference along lines passing through the centre of the field in those directions. Hence the appearance of the black cross when the tourmalines are crossed, and of the white one when their axes are parallel.

The rings are closer together in proportion as the double refraction is stronger, and the thickness of the plate greater.

The colours of the rings change, to a certain extent, according to the relative amount of double refraction for the different coloured rays. A very peculiar character, in this respect, is exhibited by apophyllite, which, as already observed, is positive for the blue, and negative for the red rays.

A plate of a biaxial crystal, cut at right angles to the median line, and placed between two tourmalines, in such a manner that the plane of the optic axes is parallel to the axis of one of the tourmalines, exhibits, when the tourmalines are crossed, the system of rings delineated in *fig.* 691. The mode of formation of the black cross is the same as that above explained with regard to uniaxial crystals. But, as the difference of path of the rays *o* and *e* increases with their inclination to both the optic axes, the rings of colour embrace both these axes. The form of these rings is nearly that of the lemniscate, a curve distinguished by the property that the product of any two radii vectores, drawn from the two poles to any point of the curve, is a constant quantity. On turning the double-refracting plate round in its own plane, the whole system of rings turns round in the same direction, and the black cross separates into two branches, presenting the appearance shown in *fig.* 692; and when the plane of the axes makes an angle of 45° with the axes of the two tourmalines, the two black bands form branches of hyperbolas, as in *fig.* 693. The general direction of the branches of the black bands is always parallel or perpendicular to the plane of primitive polarisation. On continuing the rotation of the plate from 45° to 90°, the same appearances are presented in the reverse order, and the whole series of changes is repeated in each of the four quadrants.

Fig. 691.

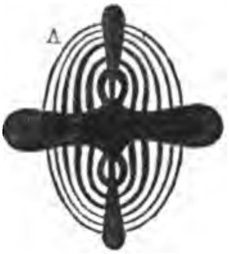


Fig. 692.

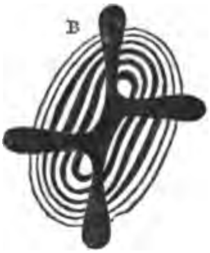
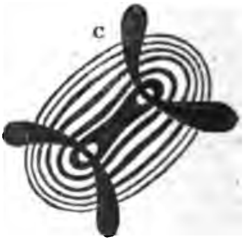


Fig. 693.

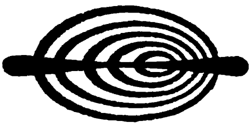


When the polariser and analyser are placed with their axes parallel, the form of the curves and of the cross are exactly the same as above, but the colours are complementary and the cross is white.

The preceding figures represent the appearance in crystals, such as nitre, which have their optic axes inclined at a small angle not exceeding 5° or 6°; when the axes are more inclined, only half the figure can be seen at once.

Fig. 694 shows the appearance of the rings formed by a biaxial crystal cut perpendicularly to one of its optic axes.

Fig. 694.



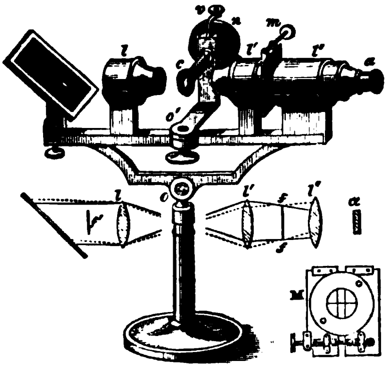
The distribution of the colours in the neighbourhood of the axes shows plainly whether the angle of inclination of the axes increases or diminishes from the violet to the red rays. The former is the case in tartrate of potassium, the latter in nitrate of potassium. In crystals of the monoclinic, as also of the di- and tri-clinic systems, even the direction of the axes of elasticity is different for the different coloured rays: thus in gypsum, diopside, and cupric formate, the position of the median line varies according to the colour. In borax, adularia, tartaric acid, and acetate of sodium, the different colours have the same median line, but differently directed ordinates, so that the planes of their axes vary with the refrangibility of the light.

The optical phenomena exhibited by many biaxial crystals are altered in a very remarkable manner by change of temperature. Glauberite, for example, is uniaxial at ordinary temperatures for violet light, but biaxial for all other colours. At lower temperatures, the violet axis also splits into two, and the angles between the axes of the other rays increase. When, on the other hand, the temperature is raised, the violet axis becomes divided in a plane at right angles to the former; the axial angles of the other colours diminish, become nothing, and then likewise pass into the perpendicular plane, in which they are all situated together, even before the temperature rises as high as the boiling point of water.

Determination of the Axes.—The form of the curves, and of the dark bands which cross them, afford the best means of determining the position of the axes in biaxial crystals. To find the position of the plane of the optic axes, the crystal, cut in the form of a plate with parallel faces, is placed between a polariser and analyser with their planes of polarisation crossed, so as to produce darkness, and the plate is turned round in its own plane till its presence does not restore the light. Two positions are thus found, for which the traces of the primitive plane of polarisation are to be marked on the crystalline plate. These two traces form a right angle, and one of them is situated in the plane of the axes. The plate is then turned round in its own plane, till each of the traces makes an angle of 45° with the primitive plane of polarisation; then, by inclining it successively round these traces, a position is sought in which the rings can be seen surrounding the axes. The plane of the axes is perpendicular to the line round which the plane has been turned to discover the rings.

Measurement of the Angle between the Axes.—The most convenient apparatus for this purpose, and for all exact measurements of the coloured rings, is that of Soleil, represented in *fig.* 695.

Fig. 695.



A beam of light, polarised by reflection from the mirror V, which may be placed at any required inclination by means of the joint *o*, passes through a lens, *l l*, and is brought to a focus on the crystalline plate *c*, where the rays cross each other and issue in diverging cones. They then pass through an eyepiece, *l'l''*, *l l''*, forming at *ff*, the focus of the lens *l*, an image of the curves produced by the plate *c*, and this image is viewed through the lens *l''* and the analyser *a*. At *ff* is placed a micrometer, *m*, represented separately at M. It has three wires, two parallel to one another, perpendicular to the third, and capable of being brought together or separated by a screw, one part of which is right-, and the other left-handed. The plate *c* is held by a socket capable of turning on a horizontal axis, its rotation being measured by a divided screw-head, *n*, and a vernier which is read off by the magnifier *v*. The support of the socket is also capable of turning on *o*, so that the crystalline plate *c* may be placed in any required position.

To measure the angle between the axes, it is best to use homogeneous light. The crystalline plate *c*, cut nearly at right angles to the median line, is fixed in the socket in such a position that the plane of its axes may be vertical, and the socket is turned round in its own plane, so as to bring each of the poles successively to coincide with the intersection of the wires of the micrometer. The arc through which the screw is turned between the two positions gives the observed angle $2\alpha'$ between the apparent optic axes (p. 664). From this the real angle between these axes is calculated by the equation $\sin\alpha' = \mu' \sin\alpha$, in which μ' is the middle of the three characteristic refractive indices for the coloured ray observed.

Soleil's apparatus serves also to measure the diameters of the rings; the micrometer being capable of turning round on itself, the diameters can easily be measured in any required direction.

Double-refracting structure produced by Molecular Tension.—Glass, gelatin, and other amorphous bodies, also crystals belonging to the regular system, acquire the double-refracting structure, when pressed, stretched, or heated unequally in different parts, and exhibit, when examined by polarised light, coloured bands similar to those produced by double-refracting crystals. A rectangular plate of glass laid edge-ways on a very hot iron plate, exhibits, when examined in a polarising apparatus, a series of coloured bands parallel to its edges, these bands altering their arrangements as the heat is gradually conducted across the plate, and disappearing altogether when it becomes uniformly heated all over. A similar effect is produced by placing the glass in the same manner on a plate of metal cooled by a freezing mixture, or by subjecting it to lateral compression.

These effects are, however, most strikingly exhibited by unannealed glass—that is to say, glass which has been heated and quickly cooled. Glass thus treated has an irregular structure, the parts near the surface having been more quickly cooled than the interior parts, and torn away from them, as it were, by the sudden contraction in cooling. In consequence of this irregularity of structure, the glass produces double refraction on all rays which traverse it, but in different degrees in its different parts, whence there results a variable coloration when the glass is viewed by polarised light. The figures produced exhibit a symmetry depending on that of the contour of the plate. A circular plate of unannealed glass, the structure of which is symmetrical round the axis, acts like a uniaxial crystal, exhibiting concentric rings, intersected by a black or white cross, according to the relative positions of the polariser and analyser. If the structure is not quite symmetrical round the axis, the rings and cross are distorted. A square plate exhibits a cross with coloured fringes in the angles. An elliptical plate exhibits a figure resembling those of biaxial crystals.

Absorption of Light by Double-refracting Crystals. Dichroïsm.

Certain coloured double-refracting crystals, when traversed by ordinary white light, exhibit different colours according to the direction of the rays with regard to their axes; thus dichroïte or iolite (ii. 320) appears of a yellowish white colour inclining to brown, or of a fine azure blue, according as the rays traverse it parallel or perpendicular to the axis; in like manner, chloride of palladium and potassium exhibits either a dark-brown, or a fine green colour; some varieties of sapphire are blue or yellowish green. Some green tourmalines appear dark brown-red when viewed along the axis.

This effect is due to the property possessed by double-refracting media, of absorbing polarised rays in different proportions according to the inclination of those rays with regard to their axes. The tourmaline absorbs completely all rays polarised in a plane parallel to its axis, and transmits them in greater and greater proportion as this axis is inclined to the plane of polarisation; moreover it absorbs all the simple rays composing white light in the same proportion, consequently the transmitted light remains always of the same colour, excepting in the case of the green tourmalines above mentioned. But when the absorption-coefficients of the several simple rays vary in different proportions with the change of direction of the rays in the crystal, the tint formed by the mixture of the unabsorbed rays likewise varies with their inclination to the axis.

Some biaxial crystals exhibit trichroïsm; thus certain Brazilian topazes of a yellowish rose tint in the direction of the median line, are violet when viewed along the complementary line, and yellowish white perpendicular to the plane of the axes.

Babinet has observed that, of the two rays into which an incident ray is divided on entering a uniaxial crystal, that which travels most slowly and is therefore most refracted, is also absorbed in the largest proportion; in positive crystals therefore, such as tourmaline, it is the ordinary, and in negative crystals, like smoky quartz, it is the extraordinary ray which is most absorbed. This law, true in the greater number of cases, nevertheless admits of numerous exceptions. Thus, Haidinger observed that the order of absorption is different in the blue and yellow varieties of beryl, although both are negative. Beer observed that acid chromate of potassium, cyanite, and certain varieties of topaz also form exceptions to the rule; and that idocrase and cupric acetate, which follow the law as regards the blue rays, deviate from it as regards the yellow, orange, and red.

Hagen has demonstrated the following laws regarding the absorption of light by double-refracting crystals.

1. The general law of the decrease of intensity in geometric progression as the thicknesses increase in arithmetic progression (p. 636), holds good for double-refracting, as well as for isophanous media, so that the ratio $o : e$ likewise varies according to the same law.

2. The ratio $o : e$ is a continuous function of λ, exhibiting, in all the crystals observed, a maximum and a minimum.

3. The variations of $o : e$ are equal on either side of the maximum or the minimum; so that if the maximum or minimum occurs at a particular wave-length λ', the values of $o : e$ for $\lambda' + n$ and $\lambda' - n$ are equal.

4. The absolute value and the position of the maximum and minimum depend upon the direction of the plate with regard to the axes of the crystal.

5. From the mode of variation of the function $o : e$, it is probable that in crystals, which form exceptions to Babinet's law, the exception applies only to certain rays of the spectrum.

Circular Polarisation.

It has already been pointed out (p. 658), that when two rays of light travelling along the same path are polarised in planes at right angles to each other, and differ in phase by a quarter of a wave-length, then if the amplitudes of vibration of the two are equal, the molecules of the resultant wave vibrate in circles transversely to the direction of the ray. In this state the ray is said to be circularly polarised, and the phenomena which it exhibits are the same as if the ray were polarised in one plane, and that plane were made to rotate round the direction of the ray as an axis.

Circular polarisation is exhibited in a remarkable manner by quartz, in which it was first discovered. A plate of this substance (which is uniaxial) cut at right angles to the optic axis, exhibits when viewed between two tourmalines or Nichol's prisms with their axes crossed, a system of coloured rings similar to those produced by calcspar (p. 668); but the centre of the field of view, instead of exhibiting a black cross, is illuminated with brilliant colours, red, yellow, green, blue, &c., according to the thickness of the plate. On turning the analyser on its axis, the colours in the centre go through the regular prismatic series from red to violet, or the contrary, according to the direction of rotation, but no alteration of colour is produced by rotating the plate of quartz while the analyser remains stationary.

To understand these phenomena, we must examine what takes place when homogeneous light is used. Suppose, then, a plate of dark red glass coloured with red oxide of copper to be interposed between the two tourmalines or Nichol's prisms, crossed as before, so that no light is transmitted by the analyser. If the plate of quartz be now interposed, a red light immediately makes its appearance, and to render the field again dark, it is necessary to turn the analyser through a certain angle, either to the right or to the left. Hence it follows that the ray which has traversed the quartz must have had its plane of vibration deflected through an angle equal to that through which the analyser has been moved.

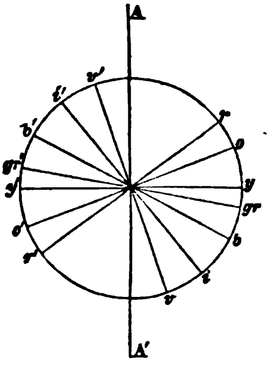
Precisely similar effects are produced with yellow, green, violet, or any other kind of homogeneous light; but the angle of rotation varies according to the nature of the ray, being least for red and greatest for violet light.

Colours.	Angle of rotation.	
	Plate 1 mm. thick.	Plate 3·75 mm. thick.
Medium red	15°	56¼°
„ orange	19	71¼
„ yellow	24	90
„ green	27	101¼
„ blue	32	120
„ indigo	38	142½
„ violet	44	165

Some crystals of quartz rotate the plane of polarisation of a ray to the right, others to the left; the former are called right-handed, the latter left-handed quartz. But in whichever direction the rotation takes place, a plate of quartz of given thickness always produces the same amount of angular deviation for a ray of given refrangibility; and for plates of different thickness the deviation for any particular ray increases in direct proportion to the thickness. The preceding table gives the angles of deviation for the principal rays of the spectrum produced by plates of quartz of the thickness of 1 millimetre and 3·75 millimetres.

Biot found by observation that the angles of rotation for the different simple colours are nearly proportional to the squares of the indices of refraction, or inversely as the squares of the wave-lengths. This law is approximately true also for most substances which exhibit circular polarisation, while some, on the other hand, exhibit remarkable deviations from it: thus an aqueous solution of tartaric acid deflects the green rays more than the violet; and an alcoholic solution of camphor, though it deflects the several coloured rays in the order of their refrangibility, produces a much greater difference of deviation between the less and the more refrangible rays than that which is indicated by Biot's law.

Fig. 696.



We can now explain the succession of colours produced when ordinary daylight is used. Suppose a beam of white light, polarised by a Nichol's prism, whose principal action is parallel to A A' (*fig.* 696), to pass through a plate of right-handed quartz, 3·75 mm. thick. The vibrations of the several coloured rays composing the beam of polarised light are all at first parallel to A A'; but by passing through the quartz, their planes of vibration are deflected through the several angles given in the above table, the red ray then vibrating in the line $r\ r'$, the yellow in $y\ y'$, the violet in $v\ v'$, &c. Now, let the ray be viewed through another Nichol's prism, placed with its principal section also parallel to A A'; then on resolving each of these vibrations into two others, one parallel and the other perpendicular to A A', it will be seen that the red and violet rays will be transmitted with but slightly diminished intensity, the orange and blue with less, the yellow still less, and the green not at all. The result will, therefore, be a purple tint. Now let the eye-piece be turned from left to right. As the principal section passes successively over the lines $r\,r'$, $o\,o'$, &c., the red, orange, yellow, &c., will, in succession, be more fully transmitted than the other rays, so that a series of tints will be produced, agreeing nearly with the colours of the spectrum and following in the same order, from red through yellow to violet. If the analyser be turned the contrary way, the order of the tints will be reversed. If the quartz were left-handed, the phenomena would be precisely similar, excepting that the colours would change from red through yellow to violet when the analyser was turned from right to left.

Similar changes of colour are produced with a plate of quartz of any other thickness; but the tint produced at any given inclination of the polariser and eye-piece is, of course, different.

The tint produced with a quartz-plate 3·75 mm. thick, when the principal sections of the polariser and analyser are parallel to one another, deserves particular notice. As already observed, it is a purple, and, moreover, it changes very quickly to red or to violet, when the analyser is turned one way or the other, the change of colour thus produced being, in fact, very much more rapid and decided than in any other part of the circuit. This peculiar tint is accordingly distinguished by the term sensitive tint, or transition tint (*couleur sensible, teinte de passage*). On account of the facility and certainty with which it may be recognised, it is frequently adopted as the standard tint in measuring the angles of rotation produced by different substances; it is, in fact, much easier to determine when this particular colour makes its appearance, than to seize the exact moment when a ray of red, yellow, or other homogeneous light completely disappears.

The rotatory power of quartz is essentially related to its crystalline form, as will be more fully explained hereafter. It is not exhibited by opal, or any other amorphous variety of silica, or by silica dissolved in potash, or fused by the oxyhydrogen blowpipe. The same is true with regard to a few metallic salts possessing the rotatory power, viz. chlorate of sodium, bromate of sodium, and sodio-uranic acetate, these salts exhibiting that power only when crystallised, not in solution.

Circular polarisation in organic bodies.—The power of rotating the plane of vibration of a polarised ray is much more widely diffused among organic than among inorganic bodies; moreover, organic substances possess it in the liquid, as well as in the crystalline state. Among organic compounds which rotate the plane of polarisation to the right, may be mentioned: Cane-sugar, glucose, diabetic sugar, milk-sugar, dextrin, camphor, asparagin, cinchonine, quinidine, narcotine, tartaric acid, camphoric acid, aspartic acid, oil of lemons, castor-oil, croton-oil. The following rotate to the left: Sugar of fruits, starch, albumin, amygdalin, quinine, nicotine, strychnine, brucine, morphine, codeine, malic acid, antitartaric acid, oil of turpentine, oil of valerian.

By passing a polarised ray through tubes of different lengths, filled with the same solution of cane-sugar, or other rotatory substance, it is found that the angle of deviation is proportional to the length of the column of liquid; and, by filling the same tube with solutions containing different quantities of sugar, &c., it is found that the angle of deviation is proportional to the quantity of the substance contained in a column of given length. Generally, then, the angle of deviation is proportionate to the number of active particles which the light has to pass.

If, then, ϵ be the quantity of active substance contained in a unit of weight of the solution, l the length of the column, and α the observed angle of rotation for a particular tint—the transition-tint, for example,—the angle of rotation for the unit of length, supposing the entire column to be filled with the optically active substance, will be $\frac{\alpha}{\epsilon l}$. But as the solution of a substance is often attended with condensation of volume, it is best, in order to obtain a measure of the rotatory power, independent of such irregularities, to refer the observed angle of deviation to a hypothetical unit of density, that is to say, to divide the quantity $\frac{\alpha}{\epsilon l}$ by the density, δ, of the solution. The fraction thus obtained, viz. $[\alpha] = \frac{\alpha}{\epsilon l \delta}$, is called the specific rotatory power, and expresses the angle of rotation which the pure substance, in a column of the unit of length and density $= 1$, would impart to the ray corresponding to the transition-tint. For example, a solution containing 155 milligrammes of cane-sugar in a gramme of liquid, has a specific gravity $= 1{\cdot}06$, and deflects the transition-tint by 24°, in a column 20 centimetres long; its specific rotatory power is therefore

$$[\alpha] = \frac{24}{0{\cdot}155 \, . \, 20 \, . \, 1{\cdot}06} = 7{\cdot}3^{\circ}.$$

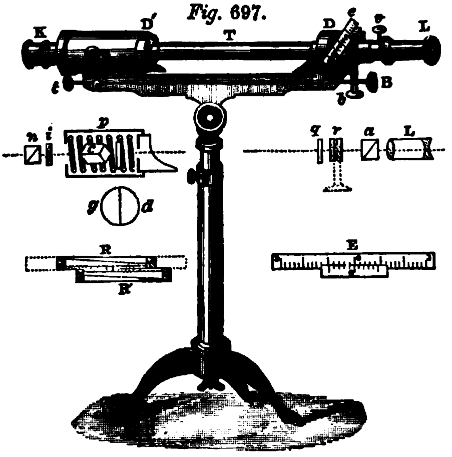
The apparatus used for measuring the rotatory power of liquids consists of a glass tube, surrounded with a case of wood or brass, and closed at both ends with plate-glass discs ground to fit water-tight, and pressed against the tube by means of screw-caps. The tube, being completely filled with the liquid, is placed on the supports, between two Nichol's prisms, one of which serves as polariser, the other as analyser. The latter carries a vernier moving round a graduated circle. The simplest way of using this apparatus is to interpose between the tube and the polariser a glass coloured with red oxide of copper, the tint of which corresponds with the red of the fixed line C of the spectrum, and, having set the analyser with its principal section at right angles to that of the polariser (which makes the field of view dark so long as the tube is not interposed), adjust the tube in its place, and turn the eye-piece round till the red light completely disappears. The angle through which the eye-piece is turned measures the deviation produced by the liquid.

The direct measurement of the rotation of the red ray is not, however, always the best mode of observation, because, as already observed (p. 672), it is difficult to tell with precision when the light completely disappears. For this purpose, there is introduced behind the polarising prism, instead of the red glass, a plate of quartz 3·75 millimetres thick, which, when the polariser and analyser are set with their principal sections parallel, exhibits the transition-tint. The interposition of the circularly polarising liquid causes this tint to change, and the rotation is measured by the number of degrees through which the prism must be turned to show the transition-tint.

Greater exactness is obtained by using a double plate of quartz 3·75 millimetres thick, one-half being composed of right-handed, the other of left-handed quartz. Such a plate exhibits the transition-tint with perfect uniformity on both halves, when the polariser and analyser are set with their principal sections parallel; but on turning the analyser to the right, one-half of the plate inclines to red, and the other to blue. The same change will, of course, take place on introducing the tube containing the circularly polarising liquid; and to restore the uniformity of tint, the analyser must be turned a certain number of degrees the contrary way. If the liquid has but a slight rotatory power, this method is quite satisfactory; but if the rotatory power is considerable, an error may arise from the different angles of rotation imparted to the different-coloured rays.

To obviate this source of inaccuracy, a contrivance called the **compensator** has been invented by Soleil, which, together with the other parts of his apparatus—called a **saccharimeter**, being especially adapted to the estimation of the strength of saccharine solutions—is represented in *fig.* 697. The tube T, containing the saccharine solution, or other liquid to be examined, is placed between two perforated diaphragms, one of which, D, is fixed, while the other, D', can be removed at pleasure to a greater distance from D, towards which it is again pressed by a spring, shown in section at *p*: this arrangement keeps the tube in position, and facilitates its adjustment. The incident light is polarised by the achromatised calc-spar prism *n*, one image of which is intercepted by a screen. At *p* is a double plate of quartz, 3·75 millimetres thick, a front view of which is shown at *g d*—one-half, *d*, being dextro-, and the other half, *g*, lævo-rotatory. The light having traversed this double quartz-plate and then the tube T, arrives at a quartz-plate, *q*, cut perpendicularly to its axis, then passes through the compensator, *r*, is analysed by the double-refracting prism, *a*, and is finally viewed through the small telescope, L L.

Fig. 697.



RR' is a horizontal section of the compensator, consisting of two quartz prisms perpendicular to the axis, and of contrary rotation to the plate *q*. These prisms can slide one over the other horizontally, and in contrary directions, so as to vary the thickness which the modified light has to traverse. They are set in motion by a toothed pinion fixed to the button *b*, and acting on two racks adapted to the lower part of the mounting of the prisms. One of these mountings carries an ivory scale, *e*, represented separately at E; the other, a vernier, which slides along the scale, and serves to measure the opposite displacements of the two prisms. When the zeros of the scale and vernier coincide, the two prisms are opposite to one another, and their thicknesses are together equal to that of the plate *q*, the rotatory power of which is therefore neutralised by them. The analyser may then be turned by means of the endless screw, *v*, into such a position, that the two halves of the double quartz-plate, *g d*, may exhibit the sensitive tint. If the tube T, containing the liquid, be then put in its place, the two halves, *g*, *d*, will then exhibit very different colours; and to restore them to equality the compensator, *r*, must be so adjusted as to produce, together with the plate *q*, an inversion opposite to that of the liquid, either by increasing the thickness of the double prism, *r*, or diminishing it, so as to allow the action of the plate *q* to predominate. The direction in which the vernier is moved along the rule, which is marked with two series of divisions on opposite sides of the zero point, indicates the direction of the rotation exerted by the liquid, and the displacement of the vernier gives the angle of deviation when the thickness of quartz corresponding to one division of the scale is known. These divisions are usually made to correspond with the tenth of a millimetre; the vernier indicates the tenth of these, so that the estimation may be made to the hundredth of a millimetre. The half of this quantity suffices to produce an appreciable difference of tint in the two halves of the double quartz-plate.

When either the light, or the liquid in the tube, is coloured, this colour, added to that produced by the polarisation, modifies the sensitive tint, and diminishes the accuracy of the observation. To neutralise this colour, Soleil places at the extremity, K, of the instrument, a double-refracting prism, *n*, and a quartz-plate, *i*, fixed in a socket, which can be turned round in its own plane by means of a toothed wheel or pinion, *t*, and the button B. This plate is interposed between the two prisms *n* and *c*, the second of which acts as analyser, and yields a colour which may be varied by turning the prism *n*, so that a position of this prism may be found which gives a tint capable of sensibly neutralising that of the liquid, or of the light employed.

As the apparatus above described requires the observation of the transition-tint, its results are exact only when applied to liquids which disperse polarised light according to the same law. Now Biot has shown that this is the case with saccharine solutions, to which, indeed, Soleil's apparatus is especially adapted; but with other liquids, such as aqueous tartaric acid, whose rotatory power for the different coloured rays does not follow Biot's law (p. 672), the observation of the transition-tint does not give good results. With such liquids it is best to resort to the simpler mode of observation previously described (p. 673), using homogeneous light.

Relation between Optical Rotatory power and Crystalline form.—Circular polarisation appears to depend on a certain want of symmetry in the molecules of the medium through which the rays pass: in fact, all crystals which exhibit circular polarisation are hemihedral or tetartohedral. This is remarkably the case with quartz, which is a combination of the opposite rhombohedrons $+R$ and $-R$ with the hexagonal prism ∞R, some varieties of it exhibiting hemihedral and tetartohedral combinations (CRYSTALLOGRAPHY, ii. 143, *fig.* 258). Moreover the six faces y $(6P\frac{6}{5})$, which are unequally inclined to those of the prism, are not always placed alike, occurring in some crystals on the right of a prismatic face above, and on the left below, and the contrary in others, as shown in *figs.* 698, 699. The two forms of crystal thus produced, though their faces are alike in number and in form, are not superposible, but one may be regarded as the reflected image of the other. The crystals of the one kind exhibit dextro-rotatory, those of the other lævo-rotatory power. The same kind of opposite tetartohedry, accompanied by a corresponding opposition of optical rotatory power, is found also in other bodies which exhibit circular polarisation.

Fig. 698.

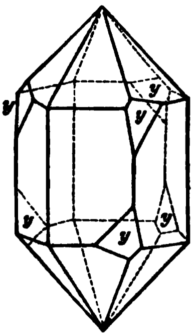
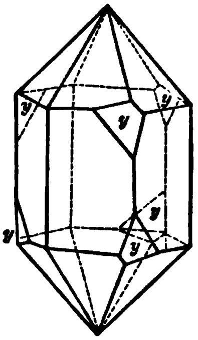


Fig. 699.



Tartaric acid and its salts turn the plane of polarisation to the right; racemic acid, which is identical in chemical composition with tartaric acid, and agrees with it in nearly all its chemical relations, has no action whatever on polarised light, either in the free state, or when combined with bases. Now, the crystals of tartaric acid and the tartrates are hemihedral; those of racemic acid and the racemates, with one exception, are holohedral. The exception alluded to is the racemate of sodium and ammonium. A solution of racemate of sodium and racemate of ammonium, in equivalent proportions, yields by evaporation, crystals of a double salt, the form of which is represented in *figs.* 700, 701.

It is a right rectangular prism, P, M, T, having its lateral edges replaced by the faces b', and the intersection of these latter faces, with the face T, replaced by a face h. If the crystal were holohedral, there would be eight of these faces, four above, and four below; but, as the figures show, there are but four of them, placed alternately: moreover, these hemihedral faces occupy in different crystals, not similar, but opposite positions; so that, as in the case of quartz, the one kind of crystal is, as it were, the reflected image of the other.

Fig. 700.

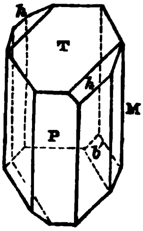
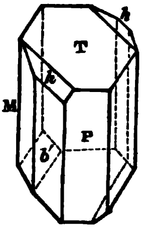


Fig. 701.



But further; by carefully picking out the two kinds of crystals, and dissolving them separately in water, solutions are obtained which, at the same degree of concentration, exert equal and opposite actions upon polarised light, the one deflecting the plane of polarisation to the right, the other, by an equal amount, to the left. Moreover, the solutions of the right and left-handed crystals, yield by evaporation, crystals, each of its own kind only; and by mixing the solutions of these crystals with chloride of calcium, calcium-salts are obtained, which, when decomposed by sulphuric acid, yield acids, agreeing with each other in composition, and in every other respect, except that their crystalline forms exhibit opposite hemihedral modifications, and their solutions, when reduced to the same degree of concentration, exhibit equal and opposite effects on polarised light.

Of the two acids thus obtained, the one which turns the plane of polarisation to the right is identical in every respect with ordinary tartaric acid; the other is called antitartaric acid. The two acids are also distinguished as dextro- and lævo-racemic, dextro- and lævo-tartaric acid. When equal weights of these two acids are dissolved in water, and the solutions mixed, a liquid is obtained, which has no action whatever on polarised light, and yields by evaporation, holohedral crystals of racemic acid. A similar result is obtained by mixing equal quantities of any of the salts of the two acids, excepting the double salt of sodium and ammonium.

Hence it appears that racemic acid, a body which has no action upon polarised light, and crystallises in holohedral forms, is a compound of two acids (tartaric and antitartaric), which have equal and opposite effects on polarised light, and crystallise in similar but opposite hemihedral forms. These acids differ also in their pyro-electric relations. The crystals of both become electric when heated, but the corresponding extremities of the two exhibit opposite electrical states. Racemic acid is not pyro-electric.

Tartaric acid may be converted into racemic acid by the action of heat, provided only it be associated with some substance which will enable it to bear a somewhat high temperature without decomposing. There are many substances whose effect on polarised light is altered by heat. This is remarkably the case with the alkaloïds of cinchona bark. When cinchonine, or any of its salts (which rotate to the right), is heated in such a manner as not to produce decomposition, it is transformed into an isomeric alkaloïd, cinchonicine, which turns the plane of polarisation to the left. Similarly, quinine, which rotates the plane of polarisation to the left, is converted by heat into quinicine, which turns it to the right. Now, when tartrate of cinchonine is heated, it is first converted into tartrate of cinchonicine, and if the heat be then continued, the change extends to the tartaric acid, half of which is converted into antitartaric acid. If the process be stopped at a certain point, and the fused mass treated with water, a solution is obtained which yields, first, crystals of antitartrate, and afterwards, of tartrate of cinchonicine. But if the heat be longer continued, the two acids unite, and form racemate of cinchonicine, from which racemic acid may be prepared, identical in every respect with ordinary racemic acid, and separable by the same means into the two opposite tartaric acids.

But, what is very remarkable, there is formed at the same time a modification of tartaric acid, which has no action whatever on polarised light, and yet is not separable into the two opposite acids. In fact, when the fused mass obtained by heating tartrate of cinchonine is treated with water, and chloride of calcium added, a precipitate is formed, consisting of racemate of calcium, and the filtrate, if left at rest, deposits crystals of the calcium-salt of inactive tartaric acid.

There are other organic compounds, which are also optically active in their ordinary forms, but exhibit inactive and inseparable modifications. Malic acid, as it exists in fruits, turns the plane of polarisation to the right; so likewise does aspartic acid, obtained by the action of acids and alkalis on asparagin. Now, both these acids may be formed from fumaric acid, an optically inactive substance. Acid fumarate of ammonium is $C^4H^3(NH^4)O^4 = C^4H^7NO^4$, which is also the formula of aspartic acid, and this acid is actually formed by heating the acid fumarate of ammonium. But the aspartic acid thus produced is, like fumaric acid, optically inactive. Again, aspartic acid is converted into malic acid by the action of nitrous acid:

$$C^4H^7NO^4 + HNO^2 = C^4H^6O^5 + N^2 + H^2O.$$

Both active and inactive aspartic acids undergo this transformation; but active aspartic acid yields active malic acid, and inactive aspartic acid yields inactive malic acid. Neither inactive aspartic nor inactive malic acid can be separated into two acids oppositely active.

Common oil of turpentine possesses considerable dextro-rotatory power; but the isomeric substance obtained by heating the artificial solid camphor of turpentine with quicklime is optically inactive.

Fusel oil has been shown by Pasteur to be a mixture of two kinds of amylic alcohol, which differ slightly in boiling point. One of these acids is optically active, the other inactive.

Circular Polarisation induced by Magnetic action.—Faraday, in 1845, made the important discovery, that bodies which, in their ordinary state, exert no particular action on polarised light, acquire the power of circular polarisation, when subjected to the influence of powerful electric or magnetic forces. A polarised ray passing along the axis of a prism or cylinder of a transparent substance, such as water or glass, has its plane of polarisation deflected to the right or left, as soon as the medium is subjected to the action of an electric current passing round it at right angles to the ray, or to that of two opposite magnetic poles (permanent or electro-magnetic), so placed that their line of junction coincides with the direction of the ray. The rotation ceases as soon as the electric or magnetic force ceases to act; its amount varies directly as the strength of the current, and its direction changes with that of the current or of the magnetic force. If the medium has a rotatory power of its own, the total effect is equal to the sum or difference of the natural and induced rotations, according as the electric or magnetic force acts with or against the natural rotatory power of the medium. (Faraday, Phil. Trans. 1846, p. 1.)

These remarkable phenomena, which led to the discovery of the universality of magnetic action, have since been followed out in greater detail by Pouillet, E. Becquerel, Wiedemann, Matthiessen, Verdet, and others.

Verdet (Ann. Ch. Phys. [3] xli. 370; xliii. 37) has confirmed Faraday's result relating to the proportionality of the rotation to the magnetic force; and has also shown that when the magnetic force acts obliquely to the ray, *the rotation of the plane of polarisation is proportional to the cosine of the angle contained between the direction of the ray and that of the magnetic action;* in other words, *the rotation is proportional to the component of the magnetic force which is parallel to the ray.* In accordance with this law, the action is greatest when the direction of the magnetic force coincides with that of the ray, and is reduced to nothing when it acts at right angles to the ray.

Direction of the rotation.—Faraday found that the direction of the induced rotation is the same as that of the acting electric current, or of an electric current which would induce the acting magnetic polarity. This law is true with regard to all diamagnetic substances; but Verdet has shown that in certain magnetic bodies the direction of the induced rotation is opposite to that of the current. This inverse or *negative* rotation is exhibited by the salts of iron, titanium, cerium, and lanthanum; whereas those of nickel, cobalt, and molybdenum exhibit *positive* rotation, that is, in the same direction as the current; while of manganese salts, some exhibit positive, others negative rotation. When a salt, such as ferric chloride, which exhibits negative rotatory power, is dissolved in water, which is positive, the negative rotation actually produced increases with the strength of the solution; the same salt dissolved in alcohol, ether, or wood-spirit, which produce much less positive solution than water, exhibits a still greater negative rotation.

Magnetic rotatory powers of different substances.—All the liquids and transparent non-crystalline solids on which Faraday experimented, exhibited more or less magnetic rotatory power. According to Matthiessen (Pogg. Ann. lxxiii. 65, 71; Compt. rend. xxiv. 969; xxv. 200), this power is not exhibited by fused phosphoric acid, flint, agate, or fluoride of calcium. Crystallised bodies in general do not exhibit it; rock-salt, however, is susceptible of it in a very high degree. Mercuric chloride, carbonate of lead, and chromate of lead are quite unsusceptible of magnetic rotatory power, when crystallised, but exhibit it strongly in the amorphous state.

Faraday's heavy glass (boro-silicate of lead) was formerly regarded as the substance most highly susceptible of magnetic rotatory power; but Matthiessen has shown that several other kinds of glass exhibit it in a still higher degree. The greatest rotatory power is exhibited by the silicates, and perhaps by the chlorides. Among bases, oxide of lead is the one which, when introduced into glass, produces the greatest increase of magnetic rotatory power; then follow the oxides of bismuth, antimony, zinc, mercury, silver. Magnesia, strontia, and baryta do not appear to exert any influence; lime, potash, and soda diminish the effect.

Bertin (Ann. Ch. Phys. [3] xxiii. 5) has obtained the following values of the magnetic rotatory powers of several substances, as compared with that of Faraday's heavy glass:

Heavy glass	100	Trichloride of phosphorus	51
Guinand's flint-glass	87	Solution of chloride of zinc	55
Matthiessen's flint-glass	89	Solution of chloride of calcium	45
Common flint-glass	53	Water	25
Stannic chloride	77	Alcohol at 36°	18
Sulphide of carbon	74	Ether	15

The dispersion of the different coloured rays by magnetic rotation in flint-glass (Bertin) and in oil of turpentine (Wiedemann), follows the same laws as in circular polarisation, produced by quartz (p. 672).

Cause of the Magnetic Rotatory action.—Faraday at first attributed the observed effects to the direct action of the magnet on the rays of light; but further research convinced him that the rotation of the plane of polarisation is due to a temporary modification in the molecular structure of the transparent medium, induced by the action of the current or magnet. In accordance with this view, it is found that any cause which interferes with molecular displacement, likewise impedes the development of the rotatory power by magnetic action: hence it is that this power is but rarely developed in crystals. The development of this power is likewise hindered by pressure, but favoured by heat, which increases the spaces between the molecules, and thereby facilitates their displacement by magnetic action. H. W.

LIGHT, CHEMICAL ACTION OF. A large number of substances suffer chemical change on exposure either to sunlight or to certain artificial sources of light; the action thus effected is said to be chemical action induced by light. The undulatory or mechanical theory of light and heat easily explains this peculiar action of light, inasmuch as this theory supposes, in accordance with the principle of the conservation of energy, that the rapid vibrations of the luminiferous ether, giving rise to what we term light, are transferred to the smallest particles of the material substance, thus producing the chemical change. Amongst the most striking effects of the chemical changes effected by the action of light may in the first place be mentioned the action by light upon the salts of silver, giving rise to all the marvellous results of photography; and secondly, the conversion of the carbonic acid gas contained in the air into its constituent elements, by plants in sunlight, a chemical decomposition upon which the whole living world depends.

The peculiar blackening which exposure to light effects upon chloride of silver was observed as early as the middle of the sixteenth century, but the explanation of the phenomenon was first given by Scheele in the year 1777 (*Von der Luft und dem Feuer*, Leipsic, 1784, p. 64). He clearly proved that when chloride of silver is exposed to light a black substance, insoluble in ammonia, but soluble in acids, is formed, whilst at the same time hydrochloric acid is set free; and hence Scheele concluded "that the blackness which the *luna cornua* acquires from the sun's light is silver by reduction." Scheele likewise proved that the variously coloured solar rays do not affect silver-salts in the same degree, and that the chloride of silver is blackened sooner in the violet than in any other of the rays. The theory of the decomposition of silver-salts by light has made but slight progress since these first experiments of Scheele, in spite of the enormous development which practical photography has attained; and even at the present day, as regards the chemistry of the photographic processes, we are unable to advance far beyond Scheele's three fundamental discoveries, (1) the production of a black powder insoluble in nitric acid, (2) the formation of free hydrochloric acid, (3) the specific activity of the violet rays.

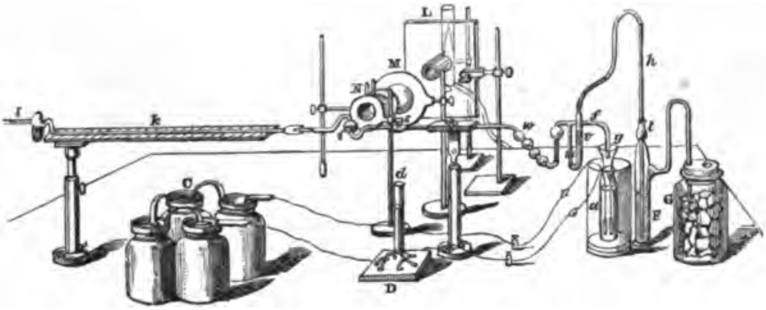
The first definite experiments made on the chemical action of light upon vegetation were those of Priestley. This acute reasoner and active experimenter showed (*Experiments and Observations on Different Kinds of Air*, Birmingham, 1790, p. 293), that it is only in presence of light that plants are able to decompose the carbonic acid of the air, assimilating the carbon, and liberating the oxygen, and thus purifying a closed atmosphere rendered impure by the respiration of animals or by the burning of a candle. These results were soon afterwards confirmed and enlarged by the labours of many chemists and botanists, amongst others by Ingenhousz, Decandolle, Saussure, and Ritter, and thus by degrees the grand relations of the atmospheric equilibrium of animal and vegetable life became apparent. It is, however, only within the last few years that the immediate dependence of all terrestrial life upon the solar radiations has been universally admitted. We now know that the animal, through the vegetable, derives its power from the sun; that it is the rapidly vibrating solar rays which are absorbed by plants and stored up in them, to be given out again in the various forms of energy, either animal or mechanical, upon the destruction of the vegetable organism by oxidation. Only the most rapidly vibrating of the solar rays are able, as a rule, to effect chemical change, and hence these violet or most refrangible rays have received the special name of the "chemical rays;" there is, however, no difference in kind between these and the other solar radiations, they all differ only in wave-lengths and in intensity of vibration.

Measurement of the Chemical action of Light.

The measurement of the chemical action of light and the investigation of the laws which regulate these important actions are subjects which have naturally attracted considerable attention. The first person who succeeded in measuring, although but roughly, the chemical action of light was Dr. Draper of New York. He employed for this purpose a reaction originally observed by Gay-Lussac and Thénard, that chlorine and hydrogen when mixed in equal volumes, do not combine in the dark, but when exposed to diffused light, gradually unite, and even combine so rapidly as to produce an explosion when placed in direct sunlight. Draper constructed an instrument by which the quantity of hydrochloric acid formed by the action of light during a given time could be approximately determined, and although the method which he employed was very incomplete, his experiments led him to the first great law of photo-chemical actions, viz., *that the chemical action of light varies in direct proportion to the intensity of the light, and to the time of the exposure.* The subject of the measurement of the chemical action of light has been placed upon an exact scientific basis by the researches of Bunsen and Roscoe. For the detailed description of the methods employed, and for many of the results which these chemists obtained, we must refer to their original memoirs (Phil. Trans. 1857, pp. 355, 381, 601; 1859, p. 879; 1862, p. 139), as we can here only give a short summary of the principles upon which their modes of measuring the chemical action of light are founded, and a statement of some of the more important results to which they have been led.

Description of the Chlorine and Hydrogen Chemical Photometer of Bunsen and Roscoe.—This instrument is founded on the same principle as the photometer of Draper, that of the combination of a mixture of chlorine and hydrogen when exposed to light, but differs from Draper's instrument in being capable of giving accurate and trustworthy measurements, inasmuch as certain necessary conditions for giving exactness to the indications are fulfilled. These consist mainly in the perfect uniformity of the gaseous mixture, constancy of pressure on the gas and liquids throughout the apparatus, and elimination of the disturbing action of radiant heat. This most delicate chemical photometer is represented in *fig.* 702. It consists essentially of three parts; namely, first the apparatus in which the sensitive gas is generated by the electrolysis of hydrochloric acid; secondly, the apparatus in which the gas is exposed to light, and thirdly, the apparatus in which the volume of hydrochloric acid produced in a given time is read off. The mixed gas, consisting of hydrogen and chlorine in equal volumes, is evolved from hydrochloric acid in the glass vessel *a* containing two carbon poles, by means of the four cells of the Bunsen battery C. By help of the gyrotrope D, the current of electricity can be greatly weakened at pleasure, and the evolution of gas in the vessel *a* reduced to a small amount. The mixed gases pass from the vessel *a* through the water contained in the washing-bulbs *w*, and thence through a horizontal tube provided with a glass stopcock *s*, into the insolation vessel *i*, in which the gases are exposed to the action of light. The lower half of this vessel is blackened to protect it from the action of the light. From the insolation vessel, the gas passes through the horizontal measuring tube *k* provided with a millimetre scale, then through the water in the vessel *l*, and finally into a cylinder filled with slaked lime and charcoal to absorb the chlorine. When the gas is allowed to pass through the apparatus, the liquids in *a*, *w*, *i* and *l* gradually become saturated with the gas; but as the saturation goes on the composition of the gas varies, and it is only after the gas has continued to pass through for three or four days that the liquids become perfectly saturated, and the mixture consists of exactly equal volumes of hydrogen and chlorine. During the process of saturation, the photochemical sensitiveness of the gas increases continually, until, when the absorptiometric equilibrium is attained, the sensitiveness reaches its maximum degree and the apparatus is ready for use. It retains this same sensitiveness for weeks, and only requires a short saturation each day previous to the actual observation. The observations are made by closing the stop-cock *s*, and allowing the light to act on the gas in the upper part of the vessel *i*. Combination then occurs, accompanied by a diminution of volume, owing to the absorption by the water of the hydrochloric acid formed, so that the atmospheric pressure forces the water in through the tube *k* towards *i*. The rate of movement of the column of water per minute gives the diminution of volume, and therefore the chemical action effected. The pressure on the gas in the jar in the insolation-vessel and measuring-tube, during the observations, is necessarily uniform, from the construction of the apparatus; but it is also necessary that uniformity of pressure be insured in all other parts of the apparatus in the intervals

Fig. 702.



between the observations; otherwise the composition of the gaseous mixture will be altered, and the results will be no longer exact. This uniformity of pressure is insured, by making the gas pass, after the stop-cock *s* is closed, through the bent tube *m v*, containing water, and thence through the tube *h*, which dips under the water in the vessel E, the pressure being regulated by raising or depressing the tube through the caoutchouc mouthpiece *t*. When the stop-cock is open the gas will pass either through the insolation vessel or through the pressure-regulator F, according to the depth to which the tube *h* is immersed in the water.

To prevent any disturbance from the effects of radiant heat (for the instrument acts as a delicate air-thermometer) the light from a coal-gas flame, or other source, having been condensed by the convex lens M, is made to pass through the cylinder N, closed with plate-glass ends, and filled with water. A screen is also placed in front of the insolation vessel to prevent radiation of heat from the body of the observer; and this, together with the screen L, serves to prevent radiation from external objects. It was found by experiment that the heat evolved by the combination of the mixed gases did not exert any sensible influence upon the results. The whole of the apparatus between *a* and *l* is connected by ground-glass joints, or by fusion, no caoutchouc or other organic substance, which could be acted upon by chlorine, being introduced, except where the waste gas is carried off. The instrument, when thus arranged, is extremely delicate; the light emitted from a small straight flame of coal-gas, 42 mm. in height, placed at a distance of 216 mm. from the insolation vessel, producing an action represented by the motion of the column of water over nearly 14 divisions of the scale in one minute. The several indications obtained agree closely with each other, and show that the instrument gives both accurate and trustworthy results. Thus the action effected by a coal-gas flame of constant dimensions on different days was as follows:

Date.	Action in 1 minute.	Difference from mean.
June 11	14·00	+ 0·01
„ 12	14·26	+ 0·35
„ 13	13·80	− 0·11
„ 19	13·83	− 0·08
„ 21	13·88	− 0·03
„ 26	13·72	− 0·19
	13·91	

Observations made with the constant flame placed at different known distances from the insolation vessel, proved that the amount of the chemical action varied inversely as the square of the distance; and experiments made in September with a flame of the same dimensions as used in June, gave results agreeing most exactly with those obtained three months previously.

Photochemical Induction.—When the gas is exposed to light, the quantity of hydrochloric acid does not at once attain the maximum. A certain time always elapses before any alteration of volume is observed; a slight alteration is, however, soon noticed, and this gradually increases until the permanent maximum is attained. This remarkable fact was first observed by Draper, who explained it by supposing that the chlorine, on exposure to light, underwent a permanent allotropic modification, in which it possessed more than usually active properties. Bunsen and Roscoe have, however, shown that neither chlorine nor hydrogen, when separately insolated, undergoes any such modification, no difference indeed being perceptible between the action of light on the gases which have been separately insolated before mixing, and on a mixture of the same gases evolved, and previously kept in the dark. The light appears, therefore, to act by increasing the attraction between the chemically active molecules, or by overcoming certain resistances which oppose their combination. This peculiar action is termed photochemical induction. The authors have fully investigated the laws of photochemical induction, and have determined the relation existing between the intensity of the light, the mass of the gas, and the duration of the inductive action; for the results thereby obtained we must, however, refer the reader to the original papers.

The resistance to combination which prevents the union of the chlorine and hydrogen gases until the action is assisted by light, is increased to a remarkable extent by the presence of even the minutest trace of foreign gases. Thus, an excess of $\frac{3}{1000}$ of hydrogen above that contained in the normal mixture reduces the action from 100 to 38. The following table shows the effect of the presence of small quantities of foreign gases upon the sensitiveness of the mixture. In each case the rate of combination of the pure gases is supposed to be 100.

Nature of foreign gas.	Volume of chlorine + hydrogen.	Volume of foreign gas.	Ratio of combination of mixture.
None	1000	0	100·0°
Hydrochloric acid	1000	1·3	100·0
Chlorine	1000	10·	60·2
		75·	50·3
		180·	41·3
Hydrogen	1000	3·	37·8
Oxygen	1000	5·	9·7
		13·	2·7
Non-insolated gas	1000	6·	55·6

The increase in the rate at which combination goes on up to a certain point, under the influence of light, appears to arise, not from any peculiarity in light, but rather from the mode of action of the chemical attractions themselves. Chemical induction is in fact observed, when there is nothing but pure chemical action to produce the change. Thus, if a dilute solution of aqueous bromine be mixed with tartaric acid and left in the dark, hydrobromic acid is formed, and the rate at which this hydrobromic acid is produced is not uniform, but increases up to a certain point, according to a law similar to that which is observed in photochemical induction. These phenomena seem to lead to the conclusion, that the chemical attraction between any two bodies is in itself a force of constant amount, but that its action is liable to be modified by opposing forces, similar to those which affect the conduction of heat or electricity, or the distribution of magnetism in steel. We overcome those resistances when we accelerate the formation of a precipitate by agitation, or a decomposition by insolation.

One of the many interesting applications of the law of photochemical induction relates to the phenomena of photography. As an instance of this application, Bunsen and Roscoe quote the remarkable observations of Becquerel, from which he assumed the existence of certain rays which can continue but not commence chemical action. In order to explain the phenomenon observed by the French physicist, it is not necessary to suppose the existence of a new property of light, as the facts are easily explained by the laws of photochemical induction (Phil. Trans. 1857, p. 400). It is probable, indeed, according to Bunsen and Roscoe, that the relations thus proved in the case of chlorine and hydrogen occur in a slightly modified form in other photochemical processes.

Comparative and Absolute Measurement of the Chemical Rays.—The first essential for the exact measurement of photochemical actions is the possession of a constant source of light. This Bunsen and Roscoe secured by employing a flame of pure carbonic oxide gas, burning from a platinum jet of 7 mm. in diameter, and issuing at a given rate and under a pressure very slightly differing from that of the atmosphere. The action which such a standard flame produces in a given time on the sensitive mixture of the chlorine and hydrogen, placed at a given distance, is taken as the arbitrary unit of photochemical illumination. This action is, however, not that which is directly observed on the scale of the instrument. The true action is obtained only by taking account of the absorption and extinction which the light undergoes in passing through the various glass-, water-, and mica-screens placed between the flame and the sensitive gas. These reductions can be made by help of the determinations detailed in the memoirs above referred to. When these sources of error are eliminated, it is possible, by means of this standard flame, to reduce the indications of different instruments to the same unit of luminous intensity, and thus to render them comparable. For this purpose, the authors define the photometric unit for the chemically active rays, as *the amount of action produced in one minute by a standard flame placed at a distance of one metre from the normal mixture of chlorine and hydrogen;* and they determine experimentally for each instrument the number of such units which correspond to one division on the scale of the instrument. By multiplying the observed number of divisions by the number of photometric units equal to one division, the observations are reduced to a comparable standard. It is proposed to call this unit a chemical unit of light, and ten thousand of them, one chemical degree of light. According to this standard of measurement, the chemical illumination of a surface, that is, the amount of chemically active light which falls perpendicularly on the plane surface, can be obtained. It has thus been found that the distance to which two flames of coal-gas and carbonic oxide, each fed with gas at the rate of 4·105 c. c. per second, must be removed from a plane surface, in order to effect upon it an amount of chemical action represented by one degree of light, was, in the case of the coal-gas flame, 0·929 metre, in that of carbonic oxide, 0·561 metre. The chemical illuminating power, or chemical intensity, of various sources of light, measured by the chemical action effected by these sources at equal distances and in equal times, can also be expressed in terms of this unit of light; and these chemical intensities may be compared with the visible light-giving intensities. In like manner, the authors define chemical brightness, as the amount of light measured photochemically, which falls perpendicularly from a luminous surface upon a physical point, divided by the apparent magnitude of the surface; and this chemical brightness of circles of zenith-sky of different sizes has been determined. Experiment shows that the chemical brightness of various sized portions of zenith-sky, not exceeding 0·00009 of the total heavens, is the same; or, that the chemical action effected is directly proportional to the apparent magnitude of the illuminating surface of zenith-sky. It is, however, possible to express photochemical actions, not only according to an arbitrary standard, but in absolute units of time and space. This has been done by determining the absolute volume of hydrochloric acid formed by the action of a fixed source of light during a given space of time; and in this way the chemical illumination of any surface may be expressed by the height of the column of hydrochloric acid which the light falling upon that surface would produce, if it passed through an unlimited atmosphere of chlorine and hydrogen. This height, measured in metres, Bunsen and Roscoe call a light-metre. The chemical action of the solar rays can be expressed in light-metres, and the mean daily or annual light thus obtained regulates the chemical climate of a place, and points the way to relations for the chemical actions of the solar rays, which in the thermic actions are already represented by isothermals, isotherals, &c.

Chemical Action of Diffuse Daylight.—In order to determine the chemical action exerted by the whole diffuse daylight upon a given point on the earth's surface, the authors were obliged to have recourse to an indirect method of experimenting, owing to the impossibility of measuring the whole action directly, by means of the sensitive mixture of chlorine and hydrogen. For the purpose of obtaining the wished-for result, the chemical action proceeding from a portion of sky at the zenith, of known magnitude, was determined in absolute measure; and then, by means of a photometer, whose peculiar construction can only be understood by a long description, the relation between the *visible* illuminating power of the same portion of zenith-sky and that of the total heavens was determined. As, in the case of lights from the same source, but of different degrees of intensity, the *chemical* actions are proportioned to the *visible* illuminating effects, it was only necessary, in order to obtain the chemical action produced by the total diffuse light, to multiply the chemical action of the zenith-portion of sky by the number representing the relation between the visible illumination of the total sky and that of the same zenith-portion. The laws according to which the chemical rays are dispersed by the atmosphere can only be ascertained from experiments made when the sky is perfectly cloudless. In the determinations made with this specially arranged photometer, care was therefore taken that the slightest trace of cloud or mist was absent, and the relations between the visible illuminating effect of a portion of sky at the zenith and that of the whole visible heavens, was determined for every half hour from sunrise to sunset, the observations being made on the summit of a hill near Heidelberg, from which the horizon was perfectly free.

The amount of chemical illumination which a point on the earth's surface receives from the whole heavens, depends on the height of the sun above the horizon, and on the transparency of the atmosphere. If the atmospheric transparency undergoes much change when the sky is cloudless, a long series of experiments would be needed before the true relations of atmospheric extinction for the chemical rays could be arrived at; the authors, however, believe that the alterations in the transparency of the air with a cloudless sky are very slight, and they think themselves justified in considering the chemical illumination of the earth's surface on cloudless days to be represented simply as a function of the sun's zenith-distance. This supposition is confirmed by experiments made on different occasions with varying zenith-distance of the sun, inasmuch as these all agree closely amongst themselves. From a series of observations made on June 6, 1858, the relation between the amount of light *optically* measured, falling from the whole sky, and the amount (taken as unity) which at the same time falls from a portion of zenith-sky equal to $\frac{1}{1000}$th part of the whole visible heavens, has been calculated for every degree of the sun's zenith-distance from 20° to 90°. These numbers multiplied by the *chemical* light proceeding from the same portion of zenith-sky for the same zenith-distance, give the chemical action effected by the whole diffuse light. The amount of chemical light which falls from the zenith-portion of sky is, however, the chemical brightness of that portion of sky. This chemical brightness was determined by the chlorine and hydrogen photometer on various days and at various hours when the sky was perfectly cloudless; thence the authors obtained the chemical action, expressed in degrees of light, which is effected on the earth's surface by a portion of zenith-sky equal in area to $\frac{1}{1000}$th part of the whole heavens, under corresponding sun's zenith-distances from 20° to 90°. The numbers thus obtained have only to be multiplied by those of the former series of observations, in order to give the chemical action effected by the total diffuse light of day for zenith-distances varying from 20° to 90°. Knowing the relation existing between the sun's altitude and the chemical action, the chemical illumination effected during each minute at any given locality at a given time may be calculated. For the following places, the amount of chemical illumination expressed in degrees of light which falls from sunrise to sunset at the vernal equinox is:

Melville Island	10,590	Heidelberg	18,220
Rejkiavik	15,020	Naples	20,550
St. Petersburg	16,410	Cairo	21,670
Manchester	18,220		

Chemical Action of Direct Sunlight.—The chemical action of the direct sunlight was determined by allowing a small but known portion of direct sunlight to fall into the dark room in which the instrument was placed, so that the insolation vessel was bathed in the pencil of rays thus admitted. By help of Silbermann's heliostat, the sun's image was reflected during the whole day upon one spot, a small opening of known size, in the window-shutter of a dark room. The fraction of the total sun's rays thus admitted and allowed to fall upon the chemical photometer was calculated, and the action thus effected was observed: hence the amount of action can be found which the sun would have produced if directly shining upon the instrument,—a condition impossible of course to fulfil, as the action would become too rapid and the whole apparatus would be shattered by explosion.

The day chosen for observation of the sun's action must obviously be cloudless, if we wish to obtain an idea of the relation existing between the chemical action and the height of the sun. Beginning the observations as near sunrise as possible, we find, for instance, on September 15, 1858, one of the days on which such a series of experiments was made, that at 7^h 9^m a.m., when the sun's zenith-distance was 76° 30′, the observed action amounted to 1·52: that is, in one minute the column of water moved through 1·52 division; or the quantity of hydrochloric acid formed, when the sun stood at the height mentioned, was represented by 1·52 division on the scale. Gradually, as the day wore on, the observed action for each minute became larger; until at 9^h 14^m a.m., the latest observation possible on the day in question, owing to the formation of clouds, the action reached 18·5 divisions, or was thirteen times as large as at 7^h 9^m. In the last column of the accompanying table is found the action, expressed in degrees of light, which would have been observed at the foregoing times, if the whole sunlight had been allowed to fall on the instrument:

Hour.	Sun's zenith-distance.	Observed action. 1 minute.	Total sun's action in degrees of light.
7^h 9^m	76° 30′	1·52	5·54
7 26	73 49	4·22	15·50
7 40	71 37	6·09	22·43
8 0	68 34	7·56	27·85
8 7	67 30	8·38	38·87
8 26	64 42	12·48	45·85
8 54	60 48	17·09	62·59
9 14	58 11	18·51	67·61

This great increase in the chemical action with the rise of the sun in the heavens results simply from the fact that the solar rays, in passing through the air, are extinguished or absorbed, lost in fact as light; and that as the sun rises higher above the horizon, the column of air through which the rays pass is constantly being lessened: consequently, more of the direct rays reach the earth.

Now, the law according to which the direct rays of the sun are thus absorbed in the air can be obtained from the experiments, of which the foregoing is only an example: hence, if the action which the sun produces, when at a given height, is known, it is possible to calculate the action which it would produce at any other height.

The law regulating the chemical action of direct sunlight may be thus expressed: The amount of chemical action effected at a point upon the earth's surface on any cloudless day, by the direct solar rays, depends alone upon the suns's zenith-distance, or upon the height of the column of air through which the rays have to pass.

That these calculated results agree very closely with the experimental data—with the observed action—is seen by comparing the numbers in Table II., expressing the observed and calculated action:

TABLE II.

Sun's zenith-distance at time of observation.	Chemical illumination of sun's direct rays at the earth's surface expressed in degrees of light.	
	Observed.	Calculated.
46° 8′	93·0	96·4
50 51	89·2	85·8
57 35	63·1	67·9
58 11	67·6	66·2
60 48	62·6	58·3
64 42	45·9	47·9
67 30	38·9	36·6
68 34	27·9	33·1
71 37	22·4	24·5
73 49	15·5	16·3
76 30	5·5	9·2
Probable error = ± 2·7 degrees of light.		

Knowing the law which regulates the absorption of the chemical rays, we can calculate what the action would be if there were no atmosphere to diminish the power of the rays. It is thus found that if the sun's rays were not thus weakened, by passage through the atmosphere, they would produce an illumination represented by 318 *degrees of light;* or they would effect a combination in one minute, upon an unlimited atmosphere of chlorine and hydrogen on which they fell perpendicularly, of a column of hydrochloric acid, 35·3 *metres in height.* The sun's rays having passed perpendicularly through our atmosphere to the sea's level, effect an action of only 14·4 *light-metres;* or three-fifths of their chemical activity has been lost by extinction and dispersion in the atmosphere.

A large number of most interesting conclusions may be drawn from the facts already noticed. Thus, for instance, we may determine the chemical action which the solar rays will produce on the various planets; for we know that the intensity of the chemical illumination varies inversely as the square of the distance of the planet from the sun. The numbers in Table III. express this chemical action in degrees of light, and in heights of columns of hydrochloric acid called *light-metres.* Hence, we see how much the sun's chemical action varies on the different planets, the superior planets receiving so small a portion as to render it impossible that the kind of animal and vegetable life which we here enjoy can there exist.

TABLE III.—*Chemical Action produced by Direct Sunlight on each Planet.*

	Mean distances.	Chemical action in Light-degrees.	Chemical action in Light-metres.
Mercury	0·387	2125·0	235·4
Venus	0·723	608·9	67·5
Earth	1·000	318·3	35·3
Mars	1·524	137·1	15·2
Jupiter	5·203	11·8	1·2
Saturn	9·539	3·5	0·4
Uranus	19·183	1·0	0·1
Neptune	30·040	0·4	0·04

Interesting conclusions can be drawn from these facts, concerning the distribution of the chemical rays on the surface of our earth in different latitudes, and at different elevations above the sea's level. The farther removed a situation is from the level of the sea, the higher up in the atmosphere it is placed, the greater is the amount of chemical action which it receives. Thus, in the highlands of Thibet, where corn and grain flourish at a height of from 12,000 to 14,000 feet, the chemical action of the direct sunlight is 1½ times as great as in the neighbouring lowland plains of Hindostan. In the same way we can calculate, for any point of the earth's surface whose latitude is known, the amount of chemical action which the direct sunlight effects at any given time of day or year. In Table IV. the numbers represent the chemical action effected by direct sunlight in one minute at the places and hours named, on the 21st of March. Curves accompany the original memoirs, showing the rise of the action with the progress of the sun through the heavens. By comparing the numbers in the table, it is seen how greatly this chemical action differs at various points on the earth's surface; and we can understand how it is, that at the latitude of Cairo, where the chemical action of the direct sunlight is twice as great as it is in that of Manchester, the whole flora and fauna assume a more tropical and luxuriant character.

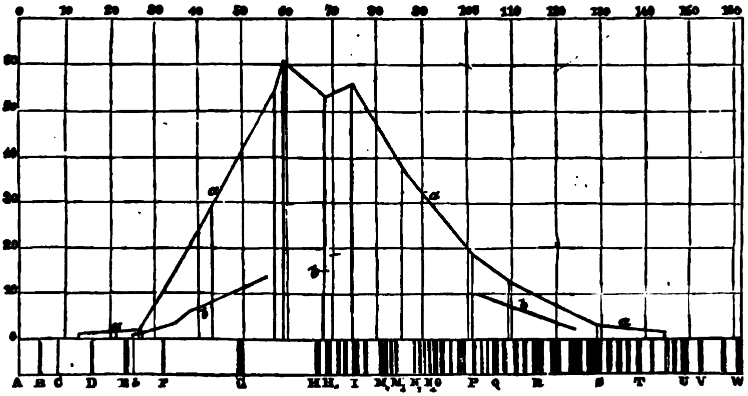
TABLE IV.—*Chemical Action effected by Direct Sunlight in One Minute on the Vernal Equinox at*

HOUR.	A.	B.	C.	D.	E.	F.	G.
6 A.M. or 6 P.M.	0·0	0·0	0·0	0·0	0·0	0·0	0·0
7 „ 5	0·0	0·02	0·07	0·22	0·38	0·89	1·74
8 „ 4	0·07	1·53	2·88	5·85	8·02	13·31	20·12
9 „ 3	0·67	6·62	10·74	18·71	23·99	35·88	50·01
10 „ 2	1·86	13·27	20·26	32·91	40·94	58·46	78·61
11 „ 1	3·02	18·60	27·55	43·34	53·19	74·37	98·33
12 at noon	3·51	20·60	30·26	47·15	57·62	80·07	105·3

A. Melville Island.
B. Rejkiavik, Iceland.
C. St. Petersburg.
D. Manchester.
E. Heidelberg.
F. Naples.
G. Cairo.

Measurement of the Chemical Action of the Constituent parts of the Solar Spectrum.—For the purpose of measuring the chemical activity of the various portions of the solar spectrum (as regards the mixture of chlorine and hydrogen), Bunsen and Roscoe reflected the sun's rays through a narrow slit, and then decomposed them by passing them through two quartz prisms. The spectrum thus produced was allowed to fall upon a white screen covered with a solution of quinine, and any desired portion of the light measured by a finely-divided scale allowed to fall upon the insolation vessel of the photometer. For the purpose of identifying the fixed lines in the lavender rays, use was made of a map of those lines made by Professor Stokes. As the various components of white light are irregularly absorbed by the atmosphere, it was necessary to make all the observations quickly one after the other, so that no appreciable difference in the column of air through which the rays passed should occur. *Fig.* 703 exhibits the chemical action effected by various portions of the spectrum on the sensitive mixture for one particular zenith-distance of the sun. Several maxima of chemical intensity in the spectrum are here noticed.

Fig. 703.



Between the lines G in the indigo, and H in the violet, the greatest amount of action was observed, whilst another maximum was found to lie near I in the ultra-violet rays. In the direction of the red end of the spectrum, the action became imperceptible about D in the orange (the maximum of visible illumination); but towards the other end of the spectrum, the action was found to extend as far as Stokes's line U, or to a distance from the line H greater than the total length of the ordinary visible spectrum.

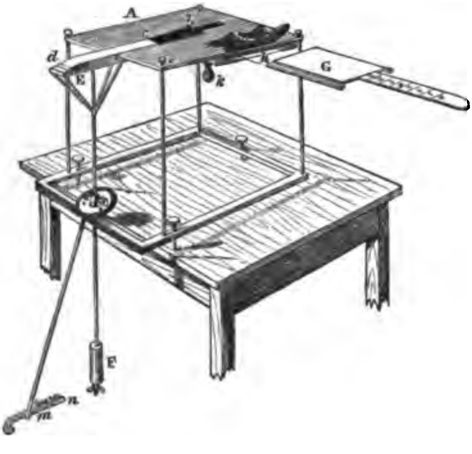
We must, however, remember that the curve which represents the amount of decomposition effected by the chemically active rays, varies according to the nature of the substance acted upon; thus Sir John Herschel showed (Phil. Trans. 1840, Part I.) that iodide of silver washed with nitrate was decomposed by ultra-violet rays which exerted no action whatever upon the chloride of silver; and whereas, in the case of the iodide, the action extends but a little beyond the line E, the action in the case of the bromide is visible to the very extremity of the visible red rays, and the maximum action on the bromide lies in the indigo rays, that of the iodide lying in the lavender rays between the lines I and M. (See also Becquerel's results, p. 632; and Daguin, *Traité de Physique*, iv. 226.)

Chemical Photometer adapted to the purposes of Meteorological Registration.—Having thus ascertained the chief laws regulating the chemical action of light, and the distribution of direct and diffuse sunlight upon the earth's surface when the sky is unclouded, Professors Bunsen and Roscoe proceeded to found a method of measuring applicable to the direct determination of the total effect produced by the varying cloud and sunshine of our changing climate. The object of this new investigation (Phil. Trans. 1863, p. 139) has been to invent a trustworthy mode of measuring the daily variation in the sun's chemical intensity, which shall be so easy and simple of practice as to be applicable to regular meteorological registration.

Although many fruitless attempts have been made to construct photometers by a comparison of the blackness produced by sunlight upon photographic paper, Bunsen and Roscoe found that the desired end could be obtained in this way by attention to certain essential conditions.

For this purpose it was necessary to construct an apparatus in which photographic sensitive paper could be exposed to sunlight for definite times measured by small fractions of a second. This instrument, called a pendulum photometer, is represented in *fig.* 704.

Fig. 704.



An iron stand carries the metal plate A, which can be placed horizontally by three set-screws, and in which a straight slit, 15 millimetres broad and 190 millimetres long, is cut. Over this slit, which is shaded black in the drawing, is placed a very thin and elastic sheet of mica, *b c d*, blackened at one end from *b* to *c*, and fastened at *d* to the curved drum E attached to the pendulum F. When the pendulum is allowed to vibrate, the sheet of mica, as it rolls on and off the curved drum E at each vibration, uncovers and again covers the slit, so that each point throughout the whole length of the slit is exposed for a different period. If we wish to use this instrument for the purpose of exposing a photographic surface to the action of the light for different times, the paper is gummed upon the white surface of the metallic slide (G, *fig.* 704); this is then covered by a metallic lid, which does not touch the paper, and the whole arrangement pushed into the dark groove *h*, placed directly under the slit, and protected from the entrance of light by a lappet of cloth, which hangs in front. The metallic lid is then withdrawn, the screw *k* turned, and thus the paper is slightly pressed against the slit, so that no light can enter sideways between the paper and the thin metallic edges of the slit. By raising the lever *n m l* at *l*, the pendulum is released from the catch at *m*, and, after completing a vibration, it is held fast by a lower catch at *n*. If it be required to double or to multiply the time of insolation, it is only necessary to repeat the vibration, once or several times, care being taken before each vibration to raise the rod of the pendulum so as to allow the end to fall into the upper catch. In order thus to set the pendulum in motion, and to stop it with certainty and ease, the lever is once for all balanced by a small weight at *l*, so that the arm *n m* is but slightly heavier than the arm *l*.

Before this instrument can be used for measuring the chemical action of light, it is necessary—

1. To know the relation existing between the several tints and the intensity of the light necessary to produce such tints.

2. To construct sensitive paper which shall always possess the same degree of sensitiveness, and can easily be prepared when required.

It was found, by a long series of experiments, that it was possible, by adhering strictly to a certain method of manipulation, to prepare standard papers which, when made, possess a constant degree of sensitiveness; so that if the same light falls upon them, the papers are always coloured to the same tint.

Experiment likewise showed that the tint attained by such a paper was constant when the *quantity* of light falling upon it also remained constant; so that light of the intensity 50 falling upon the paper for the time 1, produced the same blackening effect as light of the intensity 1 falling upon it for the time 50.

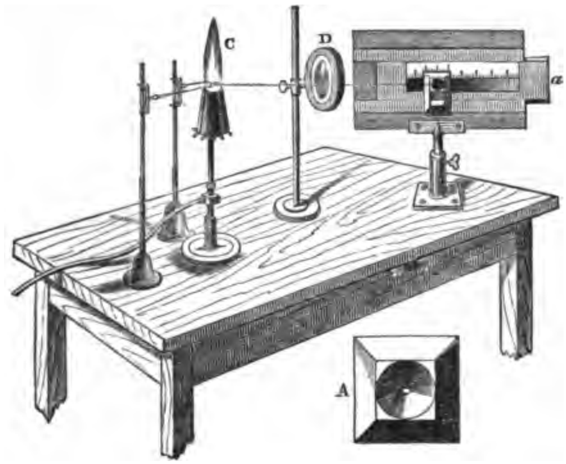
Knowing this law, which regulates the degree of shade of the paper, and having a surface of a perfectly constant degree of sensitiveness, it is easy to obtain absolute measurements of the chemical action of light. For this purpose, an arbitrary unit of measurement is chosen, by making a standard tint or paint which can be easily and exactly reproduced at any time.

The quantity of light which shall, in a second, or the unit of time, produce a blackening effect on the standard photographic paper equal to that of the standard tint, is said to have the chemical intensity 1. If the time needed to produce this same tint is found by experiment with the pendulum-photometer to be 2 seconds, then the chemical intensity is one half, and so on.

All that is needed, in order to obtain accurate measurements of the chemical action of diffuse daylight or sunlight, is to be able to find the time necessary to effect a blackening of the normal paper equal in shade to the standard tint. This is done by means of the graduated strip made in the pendulum-photometer.

For the purpose of accurately comparing these tints, the ordinary daylight, or even lamplight, cannot be used, as a change would thereby be produced on the sensitive paper. A light which does not act chemically must be used; such a light is the monochromatic soda-flame. The light from this flame possesses another advantage, namely, that the unavoidable differences of colour are not seen; variation in *shade* alone being perceptible. The arrangement for thus reading off the point having a shade equal to that of the standard tint is seen in *fig.* 705. A millimetre scale, similar to the one upon the slit, is fastened upon a wooden board, *a* (*fig.* 705), covered with paper, and moveable in a groove across a fixed wooden stand. The strip of photographically tinted paper is then cut off from the slide G and gummed upon the board *a*, so that it has the same position relative to the scale on the board as it had to the scale on the slit. A, *fig.* 706, represents a small square wooden block having a circular hole in the middle 5 to 6 mm. in diameter, the lower half being covered by the paper of which the degree of shade has to be determined. This block is pressed by means of a spring, as is seen in *fig.* 705 in a fixed position against the strip of paper. On throwing the image

Figs. 705 and 706.



of the soda-flame C, by help of the convex lens D, upon the circular opening in the block, it is easy, by drawing the slide backwards and forwards, to determine the exact point at which the upper and lower halves of the circular hole appear equally dark. It is then only necessary to read off on the scale the number representing the time which the paper at that point has been insolated, in order to determine the degree of shade which the paper in that time has attained. To ensure accuracy in the observations, it is necessary that the eye should always be placed in one and the same position; most advantageously in a direction nearly perpendicular to the surface of the strip of paper.

By help of this soda-flame, the coincidence of shade of the graduated strip with the standard tint can be read off with the greatest precision. This fact, as well as the possibility of preparing a constant sensitive paper, is seen by reference to the following tables, extracted from the detailed paper printed in the Philosophical Transactions for 1863, to which we must refer for positive proof of the delicacy and trustworthiness of the method.

Papers variously prepared were exposed for the same time to the same light.

Each reading is the mean of several observations; identity in the numbers shows identity in the shade, and, therefore, the constant sensitiveness of the papers.

The standard paper is prepared by soaking photographic paper in a solution of common salt of given strength (3 to 100), and then allowing it to lie upon the surface of a silver solution (12 nitrate of silver to 100 of water). When the strength of the salt solution varies, the sensitiveness of the paper alters very rapidly. Variation in the strength of the silver-bath produces, on the contrary, but little change in the sensitiveness of the paper.

Different qualities of paper and alterations of atmospheric moisture and temperature do not affect the sensitiveness of the paper.

1. *Effect of altering the Strength of the Silver-bath. Paper salted in a Solution containing 3 pts. Chloride of sodium to 100 of Water.*

Nitrate of silver to 100 of water.	Readings. Observer A.	Observer B.
12	128·6	129·7
10	128·7	127·0
8	128·7	128·0
6	129·7	130·0

2. *Effect of altering the Strength of the Salt Solution.*

NaCl to 100 of water.	Readings. Observer A.	Observer B.
1	2·6	60·4
2	95·7	94·6
3	132·6	129·6
4	167·0	168·0

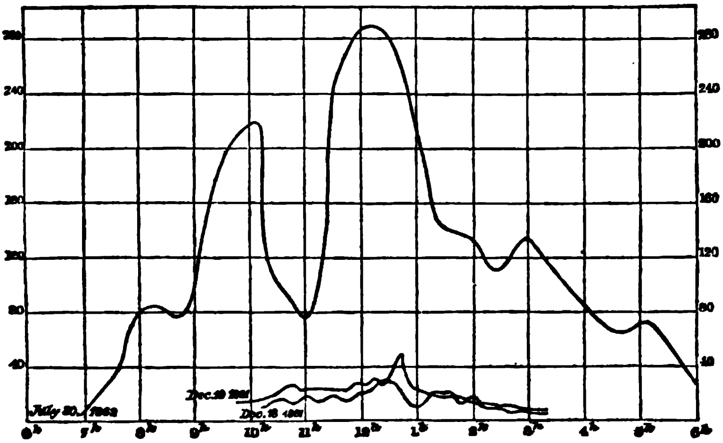
3. *Experiment showing the constant Sensitiveness of the Standard Paper.*

Paper.	NaCl to 100 of water.	Intensity No. 1.		Intensity No. 2.	
		Observer A.	Observer B.	Observer A.	Observer B.
Upper part of sheet 2	2·950	70·2	70·0	101·3	101·5
Lower part of sheet 2	3·026	70·6	69·3	101·5	101·7
Middle of sheet 1	3·026	70·0	69·5	100·9	100·9
Middle of sheet 3	3·000	70·0	70·4	101·0	100·0

All these papers were silvered in a solution containing 12 pts. of nitrate of silver to 100 of water.

In order to measure the chemical intensity of the daylight at any time, all that is needed is to expose a strip of standard paper in the pendulum-photometer for a given number of vibrations, and then to find upon the strip thus exposed the point at which a shade equal to the standard tint has been produced. Reference to a table gives the time of exposure necessary to produce this tint, and the reciprocal of this time represents the intensity of the acting light. If the time necessary were 3 seconds, the chemical intensity would be $\frac{1}{3}$; if the time were $\frac{1}{2}$ second, the intensity would be 2. In this way curves of daily chemical intensity are made, which show the variation caused by clouds, or by the changing altitude of the sun. These curves show maxima and minima exactly corresponding to the appearance and disappearance of the sun behind a cloud. The difference between the sun's chemical intensity in summer and winter is clearly seen by reference to the curves on *fig.* 707.

Fig. 707.



Based upon the principles of the pendulum-photometer, a much simpler method of making these measurements has been arranged, as follows. A graduated strip made in the pendulum-photometer is fixed in hyposulphite of sodium, and pasted upon a board furnished with a scale. The shades of certain points on this fixed strip are compared with the shades on given points upon a graduated strip prepared in the usual way, and not fixed in hyposulphite. The fixed strip is thus calibrated in terms of the unit of measurement, and it may then be used as a means of measuring the chemical action of light. Small pieces of the standard paper are then exposed for a given time to the light which it is desired to measure, until the shade approaches that of a part of the fixed strip. The point of exact coincidence is then read off by the soda flame as usual. In this way a piece of standard paper of 1 square inch of area will serve for 40 separate determinations, and the whole arrangement for exposure may be carried in the pocket. The curve of the chemical intensity of day- and sun-light in Manchester, made with this small instrument on more than 40 separate days of the year 1864, fully bears out the accuracy and ease with which these measurements can be made, and the results of his experiments induces the writer of this article to express a hope that before long these instruments may be introduced into meteorological observatories.

Chemical Brightness of various Points on the Sun's Surface.—The determination of the chemical brightness of the various portions of the sun's disc is an interesting application of this new method of photometric measurements.

By help of a camera placed on a 3-inch refractor, the writer allowed the image of the sun—of about 4 inches in diameter—to fall upon the standard paper. The sun-picture thus obtained presents interesting features: in the first place, the chemical intensity of the central portions are 3–5 times as great as that of the portions on the limb. A difference of this kind, in the case of the luminous and calorific rays, has already been observed by astronomers, and it is doubtless caused by the absorption effected by the solar atmosphere.

The following results were obtained by measuring the chemical brightness at various points on the sun's disc, on May 9, 1863; from these numbers it will be seen that the luminous intensity varies very irregularly.

CHEMICAL BRIGHTNESS OF SUN'S DISC.

1. At centre of sun's disc.		2. 15° from edge of sun's disc.			3. At the edge of sun's dis		
		N. Pole.	Equator.	S. Pole.	N. Pole.	Equator.	S. Pole.
No. 1.	100·0	38·8	48·4	58·1	18·7	30·2	28·2
No. 2.	100·0	52·8	—	56·6	30·5	—	41·0

Bright patches of considerable area were seen on the picture; these patches, which were not caused by irregularity in the paper or in the lenses, are probably owing to the presence of clouds in the luminous atmosphere of the sun, and they may probably have some intimate connection with the well-known phenomena of the red prominences seen during the solar eclipse.

Optical and Chemical Extinction of the Chemical Rays.—In order to determine whether the act of photochemical combination (in the case of chlorine and hydrogen) necessitates the production of a certain amount of mechanical effect, for which an equivalent quantity of light is expended, or whether this phenomenon is dependent upon a restoration of equilibrium effected without any corresponding equivalent loss of light, Bunsen and Roscoe have studied the phenomena occurring at the bounding surfaces, and in the interior of a medinm exposed to the chemical rays.

When light passes through any medium, part of it is lost by reflection at the surface, another portion by absorption within the medium, so that the quantity of emergent light is only a fraction of the incident light. This is true with the chemical as with the luminous rays, and Bunsen and Roscoe have determined the coefficients of absorption and reflection of the chemical rays for glass, water, and mica. By passing light from a constant source, through cylinders with plate-glass ends filled with dry chlorine, they found that, with a given length of cylinder, the quantity of chemical rays transmitted, when no chemical action takes place, is to the quantity in the incident light in a constant ratio; or in other words, the absorption of the chemical rays is proportional to the intensity of the light. They also found that the quantity of the chemical rays transmitted varies proportionally to the density of the absorbing medium. If, however, the light passes through a medium in which it is not only absorbed, but also excites chemical action, it is found that, in addition to the optical extinction already spoken of, a quantity of light is lost proportional to the amount of chemical action produced. Thus the depth of pure chlorine gas at 0° C. and 0·76 m. pressure, through which the light of a coal-gas flame must pass in order to be reduced to $\frac{1}{10}$, is found to be 173·3 mm.: hence, since the quantity of light absorbed varies as the density, the depth of chlorine diluted with an equal volume of air or other non-absorbing and chemically inactive gas required to produce an extinction of $\frac{1}{10}$ would be 346·6 mm. But when the sensitive mixture of equal volumes of chlorine and hydrogen is used, the depth of the mixture to which the light must penetrate in order to be reduced to $\frac{1}{10}$ is found only to be 234 mm. Hence Bunsen and Roscoe conclude that *light is in this case absorbed in doing chemical work.*

Light from other sources gives results similar in character, although different in amount. Diffuse light of morning reflected from the zenith of a cloudless sky is reduced to $\frac{1}{10}$ by passing through 45·6 mm. of chlorine, and through 73·5 mm. of the sensitive mixture; diffuse light is reduced to $\frac{1}{10}$ by passing through 19·7 mm. of chlorine, and through 57·4 mm. of the sensitive mixture. Hence it appears that the chemical rays of diffuse morning light are absorbed by chlorine much more quickly than those of lamp-light; and those of evening light with still greater facility. From this we may conclude that the chemical rays reflected at different times and hours, possess, not only quantitative, but also qualitative differences, similar to the various coloured rays of the visible spectrum. Photographers are well aware of this qualitative difference in the light, as they know that the amount of light photometrically estimated gives no measure of its photochemical activity; they prefer a less intense morning light to a bright evening light for taking pictures.

Photographic Transparency, or Diactinic Power of different Media.—It has already been mentioned (p. 632), that the chemical rays of the spectrum are absorbed in various degrees by different media. On this subject, some important experiments have lately been made by Professor W. A. Miller (Phil. Trans. 1863, p. 1; Chem. Soc. J. xvii. 59). The mode of observation consisted in refracting the rays which had traversed a transparent medium, through a prism and lens of quartz, and receiving them on a surface of collodion coated with iodide of silver (p. 693), whereby a permanent image of the chemical spectrum was obtained. The light employed was the electric light (obtained from an induction-coil between two metallic wires, generally of fine silver), which is peculiarly rich in chemical rays, yielding a chemical spectrum equal to four or five times the length of the visible spectrum. The following are among the most important results obtained:

1. Colourless solids which are equally transparent to the visible rays, vary greatly in permeability to the chemical rays.—2. Bodies which are photographicallly transparent in the solid form, preserve their transparency in the liquid and gaseous states.—3. Colourless transparent solids which absorb the chemical rays, preserve their absorptive action in the liquid and gaseous states.—4. Pure water is photographically

transparent, so that many compounds which cannot be obtained in the solid form sufficiently transparent for such experiments, may be subjected to trial in aqueous solution.

The following tables exhibit the photographic transparency of a few of the various solids, liquids, gases, and vapours subjected to experiment:—

Photographic Transparency or Diactinic Power of

Solids.		*Liquids*, 0·75 in.		*Gases and Vapours.*	
Rock-crystal	74	Water	74	Oxygen	74
Ice	74	Alcohol	63	Nitrogen	74
Fluor-spar	74	Dutch liquid	36	Hydrogen	74
Topaz	65	Chloroform	26	Carbonic anhydride	74
Rock-salt	63	Benzene	21	Ethylene	66
Iceland spar	63	Methylic alcohol	20	Marsh-gas	63
Sulphate of magnesium	62	Amylic alcohol	20	Hydrochloric acid	55
Borax	62	Oxalic ether	19	Coal-gas	37
Diamond	62	Glycerin	18	Benzene vapour	35
Bromide of potassium	48	Ether	16	Hydrobromic acid	23
Thin glass (0·009 in.)	20	Acetic acid	16	Hydriodic acid	15
Iodide of potassium	18	Oil of turpentine	8	Sulphurous anhydride	14
Mica (0·007 in.)	16	Sulphide of carbon	6	Sulphydric acid	14
Nitrate of potassium	16	Trichloride of arsenic	5	Air, 0·1 in. pressure	74

The photographic image obtained upon the collodion plate commenced in each case at the same point of the spectrum, corresponding with a spot a little more refrangible than the line G. Calling the line H 100, and numbering backwards for the less refrangible rays, the line B being at 84, the commencement of the photograph in each case is at 96·5, and the extreme limit of the most refrangible rays at 170·5.

When absorption occurs, it is almost always exerted upon the most refrangible rays; but in the case of the coloured gases and vapours, chlorine, bromine, and iodine, the absorption differs from the general rule, and is by no means proportional to the depth of colour. A column of chlorine, with its yellowish-green colour, cuts off the rays of the less refrangible extremity through fully two-thirds of the spectrum; the red vapour of bromine cuts off about one-sixth of the length of the spectrum, the absorbent action being limited to the less refrangible extremity, whilst the deep violet vapours of iodine allow the less refrangible rays to pass freely for the first fourth of the spectrum; then a considerable absorption occurs, and afterwards a feeble renewal of the photographic action is exhibited towards the more refrangible end.

Among the various compounds submitted to examination, the fluorides were found to be chemically the most transparent; then follow the chlorides of the alkali-metals and alkaline earth-metals; the bromides are less diactinic, and the iodides show a striking diminution in this respect. The group most remarkable for its absorptive power is that of the nitrates. Nitric acid, whether simply dissolved in water or combined with bases, has a specific power in arresting the chemical rays; the less refrangible portion it transmits freely, but intercepts the spectrum abruptly at the same points, whatever salt be employed, provided the base be diactinic. The chlorates are remarkably diactinic.

Glass, even in very thin layers, absorbs the whole of the more refrangible chemical rays. Hence it might appear that lenses of quartz, or of water enclosed in quartz, would be far superior to those of glass for the use of the photographer. This, however, is not the case; for glass is very transparent to the less refrangible portion of the chemical rays, extending beyond the violet end of the visible spectrum to a distance as much beyond the line H as the red end of the spectrum is below it; and these rays are precisely the most abundant and powerful chemical rays in the solar spectrum, which contains but few rays of refrangibility much beyond this point; whereas in the electric arc, these highly refrangible rays predominate.

Diactinic bases, united with *diactinic acids*, usually furnish diactinic salts; but such a result is not uniform: none of the silicates are as diactinic as silica itself in the form of rock-crystal. Again, hydrogen is eminently diactinic; and iodine-vapour, notwithstanding its deep violet colour, is also largely diactinic, but hydriodic acid gas is greatly inferior to either of them.

Compounds, as such, do not appear to act more energetically as absorbents than simple bodies.

Stokes (Phil. Trans. 1862, p. 606), by receiving the invisible rays upon a fluorescent screen, finds that the vegetable alkaloïds and the glucosides are, almost without exception, intensely opaque for a portion of the invisible rays, absorbing them with an energy comparable, for the most part, to that with which colouring matters, such as indigo or madder, absorb the visible rays. The mode of absorption is also generally highly characteristic of each compound, and frequently very different in the same body, according as it is examined in an acid or an alkaline solution.

The quality of the rays *reflected* from polished surfaces varies in a manner which cannot be predicted from the degree of luminosity of the surface. Gold and lead, though not the most brilliant of the metals, reflect the chemical rays more uniformly than the brilliant white surfaces of silver and speculum-metal. (Miller's *Elements of Chemistry*, 3rd ed. vol. ii. p. 899.)

Influence of Light upon Plants.

The important effects produced by sun-light on living plants has already been noticed. Many experiments have been made for the purpose of determining the action which the different portions of solar light effect upon plants during various stages of their growth. The subject is an extremely complicated one, and the results of various experimenters differ widely. Thus, for instance, whilst Payer concludes that the violet rays are those which especially determine the growth of the plant, Daubeny and Draper state, as the result of their experiments, that the yellow, or most luminous rays, are those which act most powerfully in decomposing the carbonic acid of the air. Mr. Robert Hunt[*] draws the following conclusions from his investigations on this subject:

1. The luminous rays prevent the germination of seeds.
2. The chemically active rays quicken germination.
3. Light acts to effect the decomposition of carbonic acid by the growing plant.
4. The luminous and chemical rays are essential to the formation of the colouring matter of leaves.
5. The luminous and chemical rays, independent of the calorific rays, prevent the development of the reproductive organs of plants.
6. The heat-radiations corresponding with the extreme red rays of the spectrum facilitate the flowering of plants and the perfecting of their reproductive organs.

Photography.

The first well-authenticated attempts to produce pictures by means of the chemical action of sun-light were made by Thomas Wedgwood and Sir H. Davy in the year 1802;[†] but it would appear probable from recent investigations that Boulton and Watt actually obtained sun-pictures at the Soho Works so early as the year 1799. No written statement of the method employed in their experiments has, however, as yet been found, and we must therefore still give to the former experimenters the credit of having first described a mode of obtaining pictures by the means of sun-light. The method adopted by Wedgwood was that of moistening white paper or leather with a solution of nitrate of silver. By this means he copied leaves and paintings on glass, and took profiles, and Davy even succeeded in obtaining pictures of objects seen in the solar microscope; but neither of these chemists was able to prevent the unshaded portions of the picture from being coloured by exposure to diffused light. In the year 1814 M. Nièpce examined the action of light on certain resinous substances with the object of obtaining an unalterable image in the camera. In this he succeeded to a certain extent, inasmuch as the light rendered the resin insoluble in the usual solvents, so that, by the subsequent action of an acid on the exposed metallic plate, those parts upon which the light had not fallen were etched. In 1827 M. Nièpce communicated an account of his experiments to the Royal Society, and in the same year he informed M. Daguerre, who had been previously but unsuccessfully engaged in the same pursuit, of the particulars of his process. The two investigators continued their researches in common, proposing many different modes of producing the "Heliographic pictures," as they were termed, without great success, until the death of Nièpce in 1833. Daguerre, continuing his experiments after this event with the son of Nièpce, was fortunate enough to discover, in 1839, the method which bears his name, and to obtain a prize and pension offered by the French government for the discovery of a method for permanently fixing the image formed in the camera. The process of Daguerre consisted essentially in allowing the vapour of iodine to act upon a plate of polished silver, which thus becomes coated with a thin film of iodide of silver; the plate prepared in this way was next exposed to light in the camera, so arranged that the image of the object to be copied fell upon the iodised surface, which thereby undergoes a change, not however visible on withdrawing the plate from the camera. In order to develop the latent image, the plate was exposed to the action of the vapour of mercury, which produces different effects on various parts of the plate, according as the iodide has been more or less altered by the action of the light. The undecomposed iodide was then dissolved by placing the plate in a strong solution of hyposulphite of sodium, and the picture was thereby permanently fixed. Since Daguerre's time, this process has undergone considerable improvements; amongst these, we may mention the exposure of the plate to the vapour of bromine, by which the sensitiveness of the film is greatly increased, and the reduction of metallic gold upon the surface of the film during the process of fixing, by which the lights and shades of the picture are rendered more effective. For the details of the process, as now practised, we must refer the reader to photographic text-books.

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[*] See Report by Robert Hunt "*On the present state of our knowledge of the Chemical Action of the Solar Radiation*," Brit. Assoc. Reports for 1850.

[†] Journal of Royal Institution, June 1802.

The nature of the invisible chemical change effected by the light on the iodobromide of silver is not understood, but it is evidently analogous to the change produced by the light on the mixture of chlorine and hydrogen before combination ensues, which has been termed photochemical induction, the film being so modified as to render it susceptible of decomposition when brought into contact with the vapour of mercury. The amalgam thus produced varies in thickness according to the intensity and duration of the action of the light, and different shades are therefore seen, when the picture is viewed by reflected light, corresponding to the lights and shades of the real object.

The subject of the production of sun-pictures on paper attracted but little attention from the time of Wedgwood until the year 1839, when Mr. **Fox Talbot** published his plan of "photogenic drawing." This consisted in exposing in the camera a paper soaked in a weak solution of common salt, and afterwards washed over with a strong solution of nitrate of silver; the image thus obtained was a negative one, the light being dark and the shadows light, and the pictures were fixed by immersion in a solution of common salt.

Many improvements have been made in this process. In 1841 Fox Talbot patented the beautiful process known as the "Talbotype or Calotype process," in which the paper is coated with iodide of silver by dipping it first in nitrate of silver, then in iodide of potassium. Paper thus prepared is not sensitive *per se* to the action of light, but may be rendered so by washing it over with a mixture of nitrate of silver and gallic or acetic acid. If it be exposed to the camera for two or three minutes, it does not receive a visible image (unless the light has been very strong); but still the compound has undergone a certain change by the influence of the light: for, on subsequently washing it over with the mixture of aceto-nitrate of silver and gallic acid, and gently warming it, a negative image comes out on it with great distinctness. This image is *fixed* by washing the paper with hyposulphite of sodium, which removes the whole of the iodide of silver not acted upon by the light, and thus protects the picture from further change by exposure to light. The negative picture thus obtained is rendered transparent by placing it between two sheets of blotting-paper saturated with white wax, and passing a moderately heated smoothing-iron over the whole. It may then be used for printing *positive pictures*, by laying it on a sheet of paper prepared with chloride or iodide of silver, and exposing it to the sun.

A most important step in the progress of photography is the substitution, by Mr. **Archer**, of a transparent film of **iodised collodion** spread upon glass for the iodised paper used in Talbot's process, to receive the negative image in the camera. The process is thus rendered so much more certain and rapid, and the positive pictures obtained by transferring the negative by printing on paper are found to be so much sharper in outline, than when the transference occurs through paper, as in the Talbotype process, that this method is now universally employed. In this process, as in that of the Calotype, the image produced in the camera is a latent one, and requires development with substances such as pyrogallic acid, or protosulphate of iron, which, having a tendency to absorb oxygen, induces, in presence of nitrate of silver, the reduction of the chloride or iodide to the metallic state. For a description of the best apparatus and latest processes used in the Collodion method, the reader may consult Hardwich's "Manual of Photographic Chemistry."

A large number of other metallic salts besides the salts of silver are acted upon by light. The photochemical relations of many of these salts have been specially studied by Sir **John Herschel** (Phil. Trans. 1840), in his celebrated Memoir "On the Chemical Action of the Rays of the Solar Spectrum;" and, founded upon these different actions, a number of methods of producing pictures have been described, all of which are of secondary interest. For a full description of these methods, we may refer the reader to Hunt's "Researches on Light."

Nature of the Chemical Change effected by Light on Silver Salts.—Although the exact chemical decomposition effected by light on the chloride, bromide, and iodide of silver has long been a subject of experimental discussion, still much remains to be learnt concerning the composition of the photographic image. The general result of investigations upon this subject may be stated to be that, in the first place, a sub-salt of silver of a grey or violet colour is formed, whilst by a further action of the light the silver is probably reduced to the metallic state. It appears, however,* most difficult to prepare the sub-salts of silver in a pure state, either by the action of light, or by other chemical methods, the evidence of the presence of such a salt in the violet-coloured chloride depending upon the well-known fact that this substance is unacted upon by nitric acid, but decomposed by ammonia into chloride and metal. The recent experiments of Vogel (Pogg. Ann. cxvi. 497) confirm this result, as he shows that when pure and dry chloride and bromide of silver are insolated, chlorine and bromine are liberated, and a substance insoluble in nitric acid, in each case, produced: he was unable to detect free iodine when pure iodide of silver is exposed to light, and hence he concludes that this salt is not decomposed by light. Vogel has likewise observed that the results obtained when the above-mentioned salts are prepared with an excess of silver-salt, instead of an excess of the precipitant, are somewhat different: thus, whilst the iodide prepared with excess of iodide of potassium shows no change of colour, that prepared with excess of silver becomes decidedly grey on exposure to light.

A singular effect produced by the red rays upon a blackened silvered paper was observed long ago by Ritter, and confirmed by Herschel. If prepared paper soaked in nitrate of silver solution be blackened by exposure to light, and then submitted to the action of the solar spectrum, those portions upon which the violet rays fall become darker, whilst those exposed to the red rays become lighter, and assume a brick-red colour; hence it would appear that the least refrangible rays exert opposite actions upon the sensitive silver-salts. Claudet has also shown (Phil. Trans. 1847) that exposure to the red rays neutralises the effect previously produced on a sensitised daguerreotype plate by white light.

We are as yet quite unacquainted with the essential nature of the change brought about by the action of light. Thus, we do not know whether, in the blackening of chloride of silver, the light used up in the decomposition is equivalent to the work done, as in the case of the decomposition of water by the galvanic current where the force needed to separate the molecules of oxygen and hydrogen is as large as that evolved by the combinations of the gases; or, whether the chemical actions of light resemble that sudden splitting up which occurs in certain compounds (the chloride of nitrogen, for example) where they are placed in circumstances under which they can no longer exist, and where the force establishing the change bears no equivalent relation to the forces developed in the resulting decomposition.

Chromo-photography.—Many attempts have been made to reproduce in the photograph the colours of natural bodies; and although these attempts have not succeeded to the full extent of fixing the coloured picture, yet a certain degree of progress in the production of tinted images has been made. Thus, for instance, Becquerel (Ann. Ch. Phys. [3] xlii. 81) has described a method by which a coloured image of the solar spectrum can be prepared, as well as representations of the coloured rings formed in crystals by polarised light. In order to obtain these coloured images, a polished plate of silver is immersed in dilute hydrochloric acid, and a film of sub-chloride formed upon the silver by allowing the plate to form the positive electrode of a Bunsen's battery. The plate thus prepared becomes variously tinted when exposed to the solar spectrum, some of the rays being reproduced with their distinctive colours, whilst others either produce no effect or give rise to tints differing from their own. Other experimenters, especially Nièpce de St. Victor and Campbell, have obtained somewhat analogous results; but, as yet, the coloured images produced by these and similar processes have resisted all attempts to render them permanent.

Photographic Engraving, Lithography, and Galvanography.—The original photographic process proposed in 1827 by Nièpce has been lately modified by M. Nièpce de St. Victor, for the production of photographic engraving on steel. A plate of steel is covered with a layer of prepared bitumen, and being placed under an ordinary positive photograph, is exposed to light; on treating the bitumen with naphtha and benzol, those portions which have not been insolated dissolve, leaving the steel plate exposed for the subsequent action of acid. The plate thus prepared is then submitted to the usual processes employed in aqua-tint engraving. A somewhat similar process was patented by Mr. Fox Talbot, in 1858, for etching by chemical means a positive photograph on a copper plate. This method has recently been modified and applied independently by Sir H. James and Mr. Osborne of Melbourne, to the production of lithographs and zincographs from photographs. Mr. Osborne's process consists in coating a sheet of paper with a solution of acid chromate of potassium in gelatin, and exposing the prepared paper to light by placing a negative photograph over it. After a few minutes' exposure, the paper is placed in water; the unchanged portions are then easily washed away, and those parts which have been acted upon by the light remain. This picture is then coated with lithographic ink, and transferred to the lithographic stone by pressure; the prints, obtained by transfer in the usual way, are remarkably sharp and delicate.

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* See Report on the Nature of the Photographic Image, Brit. Assoc. Reports, 1859, p. 106.

A process of photogalvanography, founded on the decomposition of gelatin and acid chromate of potassium, has likewise been proposed. The action of light on this mixture produces a change in the gelatin, rendered evident on immersing the plate in water, by a difference of level of the various parts. A mould of this raised picture is then taken in gutta percha, and a copper plate is made from the gutta-percha mould by the electrotype process; this plate is again copied by electrolysis, and from this second copper plate the prints are struck off. This process gives the means of making an infinite number of multiplications of the same subject, but the impressions obtained are not very distinct. H. E. R.

LIGNIN. Syn. with CELLULOSE (i. 818).

LIGNITE. See COAL (i. 1032) and FUEL (ii. 721).

LIGNOIN. $C^{20}H^{23}NO^{8}$.—A brown substance obtained by Reichel (*Ueber Chinarinde und deren chemische Bestandtheile*, Leipzig, 1856) from old Huanoco cinchona-bark, and further examined by Hesse (Ann. Ch. Pharm. cix. 341). It is very soluble in alkaline carbonates; the solution does not absorb oxygen from the air at common temperatures. The brown substance, boiled with caustic potash, gives off ammonia; and the substance then remaining in solution appears to have the composition $C^{20}H^{20}O^{8}$, agreeing with quinova-red and phlobaphene, and resembling a substance obtained by Reichel from red cinchona-bark. Hesse is of opinion that a brown humus-like substance, having also the composition $C^{20}H^{20}O^{8}$, and essentially different from Schwartz's cinchona-red (i. 969), is deposited in the barks of cinchona and other allied species.

LIGNONE or **XYLITE.** These names were applied to a volatile liquid of variable composition, and boiling at about 60°, obtained from crude wood-spirit by treatment with chloride of calcium, and subsequent rectification. Völckel (Pogg. Ann. lxxxiii. 272, 557) assigned to it the composition $C^{6}H^{12}O^{2}$; but the analyses made of it by other chemists, viz. Weidemann and Schweizer, Liebig, Kane, and L. Gmelin, exhibit great discrepancies (the percentage of carbon differing by about 10 per cent.), and Dancer (Chem. Soc. J. xvii. 222), by a more careful investigation of crude wood-spirit, has shown that it is a mixture, in variable proportions, of methylic alcohol, acetone, acetate of methyl, and dimethyl-acetal, $C^{4}H^{10}O^{2} = \genfrac{}{}{0pt}{}{(C^{2}H^{4})''}{(CH^{3})^{2}}O^{2}$, and that the supposed lignone or xylite has no existence. (See METHYL-ACETAL and METHYL-ALCOHOL.)

LIGULIN. See LIGUSTRUM.

LIGURITE. A mineral having the angles and character of sphene (Dufrenoy), found in a talcose rock in the Apennines.

LIGUSTRIN. See the next article.

LIGUSTRUM VULGARE. *Privet.*—The *ripe berries* of this plant contain, according to Nicklès (J. Pharm. [3] xxxv. 328), a crimson colouring matter, ligulin, soluble in water and in alcohol, either pure or etherised, but insoluble in ether. It does not contain nitrogen, is not decomposed by 48 hours' boiling with pure water, is coloured green by alkalis (Nicklès recommends this reaction for detecting acid carbonate of calcium in water), and reddened again by acids. It has not been obtained pure.

The *leaves* of privet yield, according to Polex (Arch. Pharm. [2] xvii. 75), a yellow, hygroscopic, bitter extract, called ligustrin, insoluble in ether and in absolute alcohol, but soluble in water and in dilute alcohol, forming solutions which do not give distinct reactions with any metallic salts. Strong sulphuric acid gives, with ligustrin, a deep indigo-blue colour, changing on dilution to a cornflower-blue or violet.

The leaves and bark of privet contain mannite. (Polex, *loc. cit.* Kromayer, *ibid.* ci. 281.)

LILLITE. A silicate of iron from Przibram in Bohemia, having the appearance of green earth or glauconite, and probably a product of the decomposition of iron pyrites. It is a dull, amorphous, earthy substance of blackish-green colour, and in fine powder, appearing translucent with leek-green colour under the microscope. Hardness

— about 2. Specific gravity = 3·043. A specimen, as pure as could be obtained (it is often mixed with iron pyrites and ferric hydrate), gave, by analysis, 32·48 silica, 51·52 iron and oxygen, and 10·20 water (= 94·20, including 1·96 carbonate of calcium, and 0·63 iron pyrites), agreeing approximately with the formula $(2Fe^2O.3SiO^2.H^2O).2(Fe^2)'''HO^3$.

LIMACIN. A substance obtained by Braconnot (Ann. Ch. Phys. [3] x. 319) from the garden-snail (*Limax agrestis*). When dry it forms a white earthy mass, easily crumbled between the fingers. It is somewhat soluble in cold, more soluble in boiling water, soluble in boiling alcohol, in concentrated hydrochloric acid, and easily in alkaline liquors. The solution in cold water is precipitated by tannic acid, corrosive sublimate, neutral lead-acetate, ferrous sulphate, and the acetates of copper and manganese, but not by oxalate of ammonium. By dry distillation it yields carbonate of ammonium, and leaves charcoal with a small quantity of alkaline ash.

LIMAX. According to A. Vogel and C. Reischauer (N. Jahrb. Pharm. ix. 179), many coloured snails of the genus *Limax* contain a colouring matter which appears violet in dilute acid solution, brown or black in more concentrated solution. It is obtained by macerating the animals, freed from their viscera, with dilute nitric acid, and precipitating the solution with ammonia. The brown or black iridescent precipitate is insoluble in water and in alcohol. The nitric acid solution gradually assumes a crimson colour, then becomes colourless. The colouring matter, when ignited, leaves a large quantity of phosphate of calcium.

LIMBILITE. Syn. with Chrysolite (i. 958).

LIME. Oxide of calcium (see Calcium, i. 718).

LIME, CHLORIDE OF. See Chlorine (i. 904, 908) and Hypochlorites (iii. 237).

LIME, OIL OF. $C^{10}H^{16}$.—The volatile oil of *Citrus Limetta*, obtained by distilling the torn and pressed rinds with water (i. 1003).

LIME-FLOWER, OIL OF. A volatile oil, obtained from the flowers of *Tilia europæa*, by distillation with water (Brossat, J. Pharm. vi. 396), or by exhaustion with ether in a percolator. The amount does not exceed 0·1 per cent. It is lighter than water, very volatile, and has a strong odour of lime-flowers. (Gm. xiv. 378.)

LIMESTONE. The generic name of all rocks having carbonate of calcium for their principal constituent. The principal accessory constituents are as follows:—1. Silica and alumina. The former occurs in crystalline limestones, sometimes as crystalline quartz; in compact limestones, sometimes as sand in small quantity; most frequently combined with alumina, in the form of clay. Nearly all limestones contain small quantities of clay, and in some the quantity amounts to several units per cent., the limestone then passing into marl. Limestones also occur containing silicate of calcium, as at Gjellebäk in South Norway.—2. Iron: sometimes as ferric oxide, sometimes as ferrous carbonate; generally only in small quantities and traces.—3. Manganese: either as manganic oxide or as manganous carbonate. In still smaller quantity than the iron, and often absent altogether.—4. Magnesia, as carbonate: a very frequent accessory constituent of limestones, but in true limestones not exceeding 0·5 to 1·0 per cent. When the proportion is larger, the limestone passes into dolomitic limestone and dolomite.—5. Phosphoric acid: appears to occur only occasionally, and in very inconsiderable quantity, no limestone having yet been found to contain more than 0·2 per cent. of it.—6. Alkalis, namely potash and soda, have been found in a considerable number of limestones by Schramm (J. pr. Chem. xlvii. 440) and Fehling (*ibid.* 446). Schramm found from 0·1 to 0·3 per cent. alkali, for the most part as carbonate, in smaller quantity as chloride. Fehling obtained from aluminous limestones about 3 per cent. alkaline carbonate. According to Schramm, soda always occurs in larger quantity than potash, about in the ratio of 2 at. soda to 1 at. potash.—7. Organic (bituminous) matter, probably in all limestones, excepting a few crystalline ones; sometimes in mere traces, sometimes in more considerable quantities. In anthraconite, stinkstone, and bituminous limestone, the presence of organic matter is very conspicuous.

The following enumeration of the sub-species and varieties of limestone is taken from *Ure's Dictionary of Chemistry*, and originally from *Jameson's Mineralogy*:

1. Foliated limestone; of which there are two kinds—*calcspar*, and *foliated granular limestone*. The first will be found in its alphabetical place in this Dictionary.

Granular foliated limestone.—Colour white, of various shades, sometimes spotted; massive, and in distinct angulo-granular concretions; lustre glistening, between pearly and vitreous; fracture foliated; translucent; hard as calcspar; brittle; specific gravity (of Carrara marble) 2·717. It generally phosphoresces when pounded, or when thrown on glowing coals; infusible; effervesces with acids. It is a pure carbonate of calcium. Occurs in beds in granite, gneiss, &c., and rarely in secondary rocks; it is found in all the great ranges of primitive rocks in Europe, and affords the finest marbles: Parian marble, Pentelic marble, the Marmo Greco, the white marble of Luni, of Carrara and of Mount Hymettus, the translucent white marble of statuaries, and flexible white marble, are the chief of the white marbles which the ancients used for sculpture and architecture. The red antique marble, *Rosso antico* of the Italians, and Egyptian of the ancients; the *Verde antico*, an indeterminate mixture of white marble and green serpentine; yellow antique marble; the antique Cipolin marble, marked with green-coloured zones, caused by talc or chlorite; and African breccia marble, are the principal coloured marbles of the ancients. The Scottish marbles are—the red and white Tiree, the former of which contains hornblende, sahlite, mica, and green earth; the Iona marble, harder than most others, consisting of limestone and tremolite, or occasionally a dolomite; the Skye marble; the Assynt in Sutherland, introduced into commerce by Mr. Joplin, of Gateshead: it is white and grey, of various shades. The Glentilt marble; the Balachulish; the Boyne; the Blairgowrie; and the Glenavon. Hitherto, but few marbles of granular foliated limestone have been quarried in England. The *Mona marble* is not unlike *Verde antico*. The black marbles of Ireland, now so generally used by architects, are lucullites. The Toreen, in the county of Waterford, is a fine variegated sort; and a grey marble, beautifully clouded with white, has been found near Kilcrump, in the same county. At Loughlougher, in Tipperary, a fine purple marble is found. The county of Kerry affords several variegated marbles. Of the Continental marbles, a copious account is given by Professor Jameson, *Mineralogy*, vol. ii. p. 502.

2. Compact limestone; of which there are three kinds—*common compact limestone*, *blue Vesuvian limestone*, and *roestone*.

a. Common compact limestone has usually a grey colour, with coloured delineations. Massive, corroded, and in various extraneous shapes; dull; fracture fine splintery; translucent on the edges; softer than the preceding sub-species; easily frangible; streak greyish-white; specific gravity 2·6 to 2·7. It effervesces with acids, and burns into quicklime. It is a carbonate of calcium, with variable and generally minute proportions of silica, alumina, iron, magnesia, and manganese. It occurs principally in secondary formations, along with sandstone, gypsum, and coal. Many animal petrifactions, and some vegetable, are found in it. It is rich in ores of lead and zinc, the English mines of the former metal being situated in limestone. When it is so hard as to take a polish, it is worked as a marble, under the name of shell, or *lumacoella* marble. It abounds in the sandstone and coal formations, both in Scotland and England; and in Ireland it is a very abundant mineral in all the districts where clay-slate and red sandstone occur. The Florentine marble, or *ruin marble*, is a compact limestone. Seen at a distance, slabs of this stone resemble drawings done in bistre.

b. Blue Vesuvian Limestone. Colour dark bluish-grey, partly veined with white; rolled and uneven on the surface; fracture fine earthy; opaque; streak white; semi-hard in a low degree; feels heavy. Its constituents are, lime 58, carbonic acid 28·5, water somewhat ammoniacal 11, magnesia 0·5, oxide of iron 0·25, carbon 0·25, and silica 1·25 (Klaproth). It is found in loose masses among unaltered ejected minerals, in the neighbourhood of Vesuvius. In mosaic work, it is used for representing the sky.

c. Roestone. Colours brown and grey; massive, and in distinct concretions, which are round granular; dull; opaque; fracture of the mass round granular; approaching to soft; brittle; specific gravity, 2·6 to 2·68. It dissolves with effervescence in acids. It occurs along with red sandstone and lias limestone. In England this rock is called Bath-stone, Ketton-stone, Portland-stone, and Oolite. It extends, with but little interruption, from Somersetshire to the banks of the Humber in Lincolnshire. It is used in architecture, but is porous, and apt to moulder away, as is seen in the ornamented work of the chapel of Henry VII.

3. Chalk, already described (i. 845).

4. Agaric mineral, or Rock-milk. Colour white; in crusts or tuberose pieces; dull; composed of fine dusty particles; soils strongly; feels meagre; adheres slightly to the tongue; light, almost supernatant. It dissolves in hydrochloric acid with effervescence, being a pure carbonate of calcium. It is found on the north side of Oxford, between the Isis and the Cherwell, and near Chipping Norton: as also in the fissures of limestone caves on the Continent. It is formed by the attrition of water on limestone rocks.

5. Fibrous limestone, of which there are two kinds—satin-spar, or the common fibrous; and fibrous calc-sinter. *Satin-spar.* White of various shades; massive, and in distinct fibrous concretions; lustre glistening and pearly; fragments splintery;

feebly translucent; as hard as calcareous spar; easily frangible; specific gravity 2·7. Its constituents are, lime 50·8, carbonic acid, 47·6? Stromeyer says it contains small quantities of gypsum. It occurs in thin layers in clay-slate at Alston Moor in Cumberland; in layers and veins in the middle district of Scotland, as in Fifeshire. It is sometimes cut into necklaces, &c.

Fibrous calc-sinter. Used as marble; the ancients formed it into unguent vases, the *alabaster-box* of Scripture. See CALC-SINTER (i. 720).

6. **Tufaceous limestone, or Calc-tuff.** Colour grey; massive, and in imitative shapes; enclosing leaves, bones, shells, &c.; dull; fracture fine-grained uneven; opaque; soft; feels rough; brittle. It is pure carbonate of calcium. It occurs in beds, generally in the neighbourhood of rivers; near Starly-burn in Fifeshire, and other places. Used for lime.

7. **Pisiform limestone, or Peastone.** Colour yellowish-white; massive, and in distinct concretions, which are round granular, composed of others which are very thin and concentric lamellar. In the centre there is a bubble of air, a grain of sand, or of some mineral matter; dull; fracture even; opaque; soft; brittle; specific gravity 2·532. It is carbonate of calcium. It is found in great masses in the vicinity of Carlsbad in Bohemia.

8, **Slate-spar;** *Schieferspath.* Colour white of various shades; massive, and in distinct curved lamellar concretions; lustre glistening and pearly; feebly translucent; soft; between sectile and brittle; feels rather greasy; specific gravity 2·63. Its constituents are, carbonate of calcium, with three per cent. of oxide of manganese. It occurs in primitive limestone, in metalliferous beds, and in veins. It is found in Glentilt; in Assynt; in Cornwall; and near Granard in Ireland.

9. **Aphrite** (i. 349).

10. **Lucullite;** of which there are three kinds—compact, prismatic, and foliated.

a. Compact lucullite is subdivided into common or black marble; and stinkstone.

a. The common compact. Colour greyish-black; massive; glimmering; fracture fine-grained, uneven; opaque; semi-hard; streak dark ash-grey; brittle; specific gravity 3. When two pieces are rubbed together, a fetid urinous odour is exhaled, which is increased by breathing on them. It burns white, but forms a black-coloured mass with sulphuric acid. Its constituents are, lime 53·38, carbonic acid 41·5, carbon 0·75, magnesia and oxide of manganese 0·12, oxide of iron 0·25, silica 1·13, sulphur 0·25, chloride and sulphate of potassium with water 2·62 (John). It is said to occur in beds in primitive and older secondary rocks. Hills of this mineral occur in the district of Assynt in Sutherland. Varieties of it are met with in Derbyshire; at Kilkenny; in the counties of Cork and Galway. It is the *Nero antico* of the Italians.

β. Stinkstone or *Swinestone.* Colour white of many shades, cream-yellow, grey, black, and brown; massive, disseminated, and in distinct granular concretions; dull; fracture splintery; opaque; semi-hard; streak greyish-white; emits a fetid odour on friction; brittle; specific gravity 2·7. The same chemical characters as the preceding. Its constituents are, 88 carbonate of calcium, 4·13 silica, 3·1 alumina, 1·47 oxide of iron, 0·58 oxide of manganese, 0·30 carbon, 0·58 lime; sulphur, alkali, salt, water, 2·20 (John). It occurs in beds, in secondary limestone, alternating occasionally with secondary gypsum and beds of clay. It is found in the vicinity of North Berwick, resting on red sandstone, and in the parish of Kirbean in Galloway. It is employed for burning into lime.

b. Prismatic lucullite. Colours black, grey, and brown; massive, in balls, and in distinct concretions; external surface sometimes streaked, internal lustre shining; cleavage threefold; translucent on the edges; semi-hard; streak grey; brittle; when rubbed it emits a strongly fetid urinous smell; specific gravity 2·67. When its powder is boiled in water, it gives out a transient hepatic odour. The water becomes slightly alkaline. It dissolves with effervescence in hydrochloric acid, leaving a charcoaly residuum. Its constituents resemble those of the preceding. It occurs in balls, in brown dolomite, at Building-hill near Sunderland. It was at one time called *madreporite.*

c. Foliated or *sparry lucullite.* Colours white, grey, and black; massive; disseminated and crystallised in acute six-sided pyramids; internal lustre glimmering; fragments rhomboidal; translucent; semi-hard; brittle; emits on friction a urinous smell; specific gravity 2·65. In other respects similar to the preceding. It is found in veins at Andreasberg in the Hartz.

11. **Marl;** of which there are two kinds, earthy and compact. *Earthy marl* has a grey colour; consists of fine dusty particles, feebly cohering; dull; soils slightly; is light; effervesces with acids; and emits a urinous smell when first dug up. Its constituents are, carbonate of calcium, with a little alumina, silica, and bitumen. It occurs

in beds in the secondary limestone and gypsum formations in Thuringia and Mansfeld. *Compact marl* has a grey colour; is massive, vesicular, or in flattened balls; contains petrifactions; dull; fracture earthy, but in the large masses slaty; yields to the nail; opaque; streak greyish-white; brittle; feels meagre; specific gravity 2·4. It intumesces before the blowpipe, and melts into a greenish-black slag. It effervesces with acids. Its constituents are, carbonate of calcium 50, silica 12, alumina 32, iron and oxide of manganese 2 (Kirwan). It occurs in beds in the secondary floetz limestone. It is frequent in the coal-formations of Scotland and England.

12. Bituminous marl-slate. Colour greyish-black; massive, and frequently with impressions of fishes and plants; lustre glistening; fracture slaty; opaque; shining streak; soft; sectile; frangible; specific gravity 2·66. It is said to be carbonate of calcium, with albumin, iron, and bitumen. It occurs in floetz limestone. It frequently contains cupreous minerals, petrified fishes, and fossil remains of cryptogamous plants. It abounds in the Hartz. (Jameson.)

LIMETTIC ACID. $C^{11}H^8O^6$ (H. Vohl, N. Ber. Arch. lxxiv. 16).—An acid produced, together with formic and acetic acids, by treating oil of lime, or oil of rosemary, with acid chromate of potassium and sulphuric acid. As soon as the action is finished, the liquid is diluted with water, and the limettic acid, which separates as a resin, is washed and purified by repeated solution in aqueous carbonate of potassium, precipitation with nitric acid, and recrystallisation from alcohol.

Limettic acid is white, crystalline; volatilises when heated, and forms a crystalline deposit on cold bodies. It has neither taste nor smell; dissolves sparingly in *water*, easily in *alcohol*.

The *silver-salt*, $C^{11}H^6Ag^2O^6$, obtained by adding nitrate of silver to the acid neutralised with ammonia, forms a powder sparingly soluble in water and blackening on exposure to light.

LIMONIN. The bitter principle contained in the pips of oranges and lemons. It forms small, bitter crystals, sparingly soluble in water, ether, and ammonia; easily in alcohol, acetic acid, and potash; from the potash-solution it is precipitated by acids. Sulphuric acid dissolves it, forming a red liquid, from which the limonin is precipitated by water. Nitric acid dissolves it without alteration. It melts at 124°, and solidifies to an amorphous mass on cooling. According to Schmidt's analysis (calculated with the old atomic weight of carbon), it contains 66·04—65·62 per cent. carbon, and 6·32—6·49 hydrogen, whence Schmidt deduced the formula $C^{22}H^{30}O^{13}$. (Bernays, Buchner's Rep. [3] xxi. 306.—Schmidt, Ann. Ch. Pharm. li. 338.)

LIMONITE. *Brown Hæmatite. Hydrous Sesquioxide of Iron.* (See IRON, OXIDES OF, p. 395.)

LINARITE. $Pb^2SO^4.2CuHO$. *Cupreous Sulphate of Lead. Cupreous Anglesite. Bleilasur. Kupferbleispath.*—Occurs in crystals belonging to the monoclinic system. Specific gravity 5·2—5·5. Hardness 2·5—3. Lustre vitreous or adamantine. Colour deep azure-blue. Streak pale blue. Translucent. Fracture conchoïdal. Analysis by Brooke, 75·4 sulphate of lead, 18·0 oxide of copper, 4·7 water = 98·1; by Thomson, 74·8 sulphate of lead, 19·7 oxide of copper, and 5·5 water. It occurs at Leadhills, also at Roughten Gill in Cumberland, in crystals sometimes an inch long; at Linares in Spain, and near Ems. It occurs altered to cerusite, a change like that of anglesite to cerusite. (Brooke, Ann. Phil. [2] iv. 117.—Thomson, Phil. Mag. 1840; see p. 402.—Dana, ii. 391.)

LINCOLNITE. See STILBITE.

LINDACKERITE. A mineral consisting of arsenite of copper with basic sulphate of nickel, and water; and containing, according to Lindacker's analysis (Jahrb. K. K. Geol. Reichs. iv. 552), 28·58 As^2O^3, 6·44 SO^3, 16·15 Ni^2O, 2·90 Fe^2O, and 9·32 water (= 99·73), agreeing nearly with the formula $4AsCuO^3.Ni^2SO^4.2Ni^2O.8H^2O$. Specific gravity 2—2·5. Hardness 2—2·5. Lustre vitreous. Colour verdigris to apple-green. Streak pale green to white. It dissolves after longer heating in hydrochloric acid. (Dana, ii. 500.)

LININ. A crystallisable substance from *Linum catharticum* (Pagenstecher, Ann. Ch. Pharm. xl. 322.—Handw. d. Chem. iv. 924). According to C. Schröder (N. Repert. Pharm. x. 11), the best mode of preparing it is to digest a considerable quantity of the plant with dilute milk of lime; mix the filtered yellow liquid with hydrochloric acid, which forms a precipitate remaining suspended in the liquid; agitate with ether, and leave the linin to crystallise from the ethereal solution. It forms small white crystals, having a silky lustre, heavier than water, dissolving very sparingly in water, very easily in alcohol and ether, somewhat less easily in acetic acid and in chloroform. The aqueous solution tastes slightly, the alcoholic solution intensely and persistently bitter. Linin melts and decomposes when heated. It gives by analysis 62·92 per cent. carbon and 4·72 hydrogen; does not evolve ammonia when boiled with milk of lime.

LINNÆITE. Native sulphide of cobalt.

LINOLEIC ACID. *Papaveroleic acid. Trockenölsäure.*—$C^{16}H^{28}O^2$. (Pelouze and Boudet, Ann. Ch. Phys. [2] lix. 43.—Laurent, *ibid.* lxv. 150 and 298.—Liebig, Ann. Ch. Pharm. xxxiii. 113.—Sacc, *ibid.* li. 214.—Schüler, *ibid.* ci. 252.—A. C. Oudemanns, Jun. Scheik. Onderzoek. i. Stuk. 184.—Gm. xvi. 306).—An oily acid occurring in linseed and poppy oils, and perhaps also in other drying oils. To prepare it, linseed oil (or poppy oil) is saponified, and the soap purified by repeated salting out, after which it is dissolved in a large quantity of water, and thrown down by an excess of chloride of calcium. The precipitated calcium-salt is washed, pressed, and digested in ether, which dissolves out the linoleate of calcium, and leaves the salts of the solid fatty acids undissolved. The ethereal solution is decomposed by cold hydrochloric acid, whereby the linoleic acid is separated, and remains dissolved in the ether; the solution is drawn off, and the ether distilled at as low a temperature as possible, in a stream of hydrogen. There then remains dark-yellow linoleic acid, which is dissolved in alcohol, and precipitated by ammonia and chloride of barium. The barium-salt, after being washed and pressed, is dissolved in ether, and the warts and granules, gradually formed in the solution, are repeatedly recrystallised from ether. From the barium-salt the acid is separated by agitating with ether and hydrochloric acid, pipetting off the ethereal layer of liquid, and distilling off the ether; it is dried in a vacuum over oil of vitriol and a mixture of lime and sulphate of iron (Schüler). A similar method is employed by Oudemanns, who, however, prefers precipitating the linoleate of sodium by chloride of calcium in a strongly ammoniacal solution. Sacc digests linseed oil with oxide of lead and water, at a gentle heat; exhausts the pale-grey, greasy soap with ether, which leaves margarate (palmitate according to Schüler) and a little basic linoleate of lead undissolved; evaporates the ethereal solution; and decomposes the residue with hydrochloric acid. The acid thus obtained is washed with boiling water, dissolved in ether, and recovered by evaporating the solution. Or he decomposes the lead-salt with sulphydric acid, and extracts the linoleic acid with ether.

Properties.—Linoleic acid is a faint-yellow, limpid oil, of specific gravity 0·9206 at 14°, having a high refractive power, and a weak acid reaction. It does not solidify at 18°; tastes mild at first, afterwards harsh (Schüler). It is more limpid than poppy oil (Oudemanns). It is insoluble in *water*, but dissolves readily in *ether*, less easily in *alcohol*.

Decompositions.—1. On standing in the *air* for ten weeks, the acid absorbs 2 per cent. oxygen, and becomes viscid and tough (Schüler). It takes up more oxygen the fresher it is, and thickens, so that at last it will scarcely flow, but remains colourless, and does not evolve carbonic acid (Oudemanns). A thin layer on wood exposed to the air forms a varnish; on glass it only becomes tough (Schüler). Linoleate of potassium or sodium, containing an excess of alkali, exposed in the finely divided state to the air, absorbs oxygen greedily, and becomes yellow and dry; it then dissolves in water with dark brown-red colour, and deposits, on addition of hydrochloric acid, a brown greasy resin, similar to that produced by the action of nitric acid (Sacc).—2. By *dry distillation*, products are formed, different from those yielded by oleic acid (Laurent).—3. With *nitric acid*, the acid swells up considerably, and yields a greasy resin, suberic acid, and a little oxalic acid, the last probably derived from adhering ether (Sacc). *Nitrous acid* and *mercurous nitrate* do not form elaidic acid with linoleic acid. (Pelouze and Boudet; Laurent; Schüler; Oudemanns.)

Linoleates.—The mono-acid salts are difficult to obtain pure, and generally contain too small a proportion of base, on account of their easy conversion into acid salts (Schüler, Oudemanns). They are white, for the most part uncrystallisable, and separate from their hot solutions in flakes; by spontaneous evaporation they are obtained in the form of a jelly. When exposed to the air, they become coloured and odorous. They are soluble in alcohol and ether. (Oudemanns.)

Barium-salt.—The salt produced by mixing chloride of barium with the acid to which a large excess of ammonia has been added, contains a proportion of baryta, varying from 12·04 to 24 per cent. ($C^{16}H^{27}BaO^2$ = 23·46 per cent. Ba^2O). It is white; separates from alcohol on cooling in microscopic crystals, and from ether on spontaneous evaporation, in more distinct crystals. When exposed to the air, or when kept, and also on boiling with alcohol, it becomes yellow and sticky. It dissolves very easily in ether, less easily in alcohol; and is insoluble in water. (Oudemanns).

The *calcium-salt* resembles the barium-salt. It was only once obtained of the composition $C^{16}H^{27}CaO^2$ (containing 9·72 per cent. Ca^2O), and mostly contained a smaller proportion of lime. (Oudemanns.)

The *cupric salt* is bluish-green, insoluble in water, and nearly so in alcohol. (Oudemanns.)

Lead-salt.—The acid dissolves a large quantity of oxide of lead, and forms therewith a solid, plaster-like mass; with a smaller quantity of oxide of lead it forms a thick liquid which, on exposure to the air, remains for a long time greasy, and of the consistence of ointment (Liebig). The ethereal solution of the lead-salt becomes resinised during evaporation, and throws down a white basic salt, upon which an acid, red-brown, jelly-like salt is deposited; this last smells like linseed-oil, and shows a varying composition on analysis. Exposed to the air in thin layers upon wood, linoleate of lead does not form a varnish, but strips off in scales. (Sacc.)

The *magnesium-salt* is insoluble in water.

Silver-salt.—Nitrate of silver throws down, from the sodium-salt, a white precipitate, which easily blackens from reduction of silver. It dissolves readily in aqueous ammonia, and, on evaporating the solution, a portion crystallises out; another portion is decomposed and colours the liquid black. (Oudemanns.)

Sodium-salt.—When the acid is dissolved in caustic soda, salted out with chloride of sodium, and dried, and the residue is freed from chloride of sodium by dissolving it in ether and evaporating the solution, an acid salt is obtained containing 7·5 per cent. Na^2O, and agreeing with the formula $2C^{16}H^{27}NaO^2.C^{16}H^{28}O^2$; by calculation, 7·75 per cent. Na^2O.

The *zinc-salt* is insoluble in water.

LINSEED. The seed of the flax plant (*Linum usitatissimum*). The following analyses of it are given by Way (Journ. Roy. Agr. Soc. x. pt. 2.):

Composition of Linseed.

	Nitrogen, per cent.	Fat, per cent.	Ash, per cent.	Water, per cent.
From Riga	3·60	34·70	5·25	9·45
„ Memel	3·33	36·00	3·56	8·74
„ the Black Sea	3·31	38·42	5·64	10·22
English, 1847	4·60	36·66	2·68	12·33
„ „	5·28	32·77	3·30	11·00
„ „	4·25	33·50	4·08	10·58
„ 1848	4·29	38·11	4·03	8·57

33 samples of oil-cake, obtained by expressing the fixed oil from linseed grown in various countries, exhibited an amount of nitrogen varying from 3·92 to 5·25 per cent., fat from 6·60 to 15·32 per cent., ash from 5·45 to 22·66 per cent, water from 6·56 to 10·26 per cent. The quantity of albuminous substances calculated from that of the nitrogen varies in the 33 samples from 25 to above 36 per cent.

Anderson (Highland Agr. Soc. J. new series, No. 69, p. 376) found in linseed, 24·44 albuminous substance; 34·00 oil; 30·73 gum, sugar, and cellulose; 3·33; ash and 7·50 water.

Meurein (J. Pharm. [3] xx. 96) has analysed the several parts of linseed with the following results:

Episperm 21	Gum and soluble salts	14
	Soft resin and fixed oil	1
	Water	2
	Matter insoluble in water and in ether	4
Endosperm 23	Soft resin and fixed oil	6
	Water	2
	Matter soluble in water	3
	Matter insoluble in water and in ether	12
	Fixed oil	30
	Water	5
	Matter soluble in water	3
	Matter insoluble in water and in ether	18
		100

For analysis of the ash of linseed, see FLAX (ii. 657).

Linseed also contains a large quantity of mucilage, which is deposited in the outer layers of cells of the epidermis, and swells up when the seed is macerated with water, so much as to burst the cell-walls. 1 pt. of linseed boiled with 16 pts. water yields a mucilage thick enough to be drawn out into threads, and forming a dark-coloured mass when dry. This crude mucilage contains, in addition to the true vegetable mucilage, also legumin, albumin, an organic acid, perhaps malic acid, and ash-constituents, chiefly lime, potash, and iron, partly as phosphates, partly united in the ash with carbonic acid. Linseed mucilage, precipitated by alcohol, gave 11 per cent. ash, containing 4 per cent. carbonic acid (Schmidt, Ann. Ch. Pharm. li. 29). See MUCILAGE.

LINSEED OIL. The fixed oil expressed from the seeds of *Linum usitatissimum* may be taken as the type of the class of oils called drying oils, from their property of drying up, when exposed to the air, to a transparent resinous, not brittle mass. They probably all resemble linseed oil in containing a glyceride of linoleic acid, together with palmitin (and perhaps stearin), by the varying proportions of which their differences are determined. In the impure state, they contain also mucus, gum, and albumin, together with a yellow colouring principle possessed of taste and smell.

The cold-pressed oil of fresh linseed is pale yellow, and without disagreeable taste. The commercial oil is dark yellow, and has a sharp penetrating smell and taste. Specific gravity at 13° = 0·9347 (Schüler, Schübler), 0·9337 (van Kerchoff, Jahresber. 1859, p. 701); other statements vary between 0·928 and 0·953. Specific gravity at 12° = 0·9395; at 25° = 0·931; at 50° = 0·9125; at 94° = 0·8815, that of water at 15° being taken as unity (Saussure). It does not solidify at – 15° to – 16° (Gusserow), nor at – 28° (Brandis); according to Schüler, it deposits a little solid fat at – 18°. It contains, on an average, 78·11 per cent. C, 10·98 H, and 10·93 O (Sacc); the cold-drawn oil contains, on an average, 75·17 per cent. C, 10·98 H, and 13·85 O, corresponding to the formula $C^{15}H^{26}O^2$ (Lefort). (See Saussure's analysis, Ann. Ch. Phys. [2] xiii. 338.)

It contains margarin (palmitin, according to Schüler; stearin, according to Unverdorben), and a glyceride of linoleic acid (Sacc). By saponification, it yields $\frac{1}{10}$th margarate, and $\frac{9}{10}$ths linoleate of lead (Gusserow, Kastn. Arch. xix. 80).

Linseed oil exposed to sunshine for some weeks, in contact with an aqueous solution of an equal weight of protosulphate of iron, becomes limpid and colourless. Exposed to the air in thin layers, it dries up to a transparent, resinous, moderately elastic mass, resembling caoutchouc; when heated, however, it does not melt, but carbonises and burns (Leucho, Kastn. Arch. iii. 107). A peculiar fat is produced at the same time, together with a crumbly substance, insoluble in ether (Hoppe, J. pr. Chem. lxxx. 117). Mixed with chalk so as to form a powder, and exposed to the air for four weeks, it dries up completely, and on dissolving out the carbonate of calcium with hydrochloric acid and exhausting the residue with ether, a white mass of the consistence of tar is obtained, which behaves like oleic acid altered by exposure to the air. There remains behind resinous linseed oil in the form of a yellowish conglomerate mass, which is insoluble in alcohol, ether, volatile and fixed oils, is converted by alcoholic hydrochloric acid into a tarry substance, and dissolves in caustic potash (Unverdorben, Schw. J. xvii. 245).

Impure oil, containing mucus or albumin, becomes rancid in the air, more quickly in sunshine, and has then a repulsive odour and taste, a dark colour, and acid reaction. Concerning the formation of ozonised oxygen in the oxidation of linseed oil, see Schönbein (J. pr. Chem. lxxiv. 338). When the oil is boiled for some time, till it loses about $\frac{1}{8}$ of its weight, it becomes thicker, tenacious, and viscid, and dries up still more readily than in the fresh state to a tough, turpentine-like mass, scarcely soluble in oils: *Printers' varnish.* (See INK, p. 272.)

Linseed oil (also nut or poppy oil), heated to about 323°—375°, takes fire and burns quietly, without further heating from without, till tar or charcoal remains. If the burning be interrupted by closing the vessel, there remains a brown, turpentine-like body which may be used as *birdlime.* When this substance is boiled continuously with water containing nitric acid (water being added to prevent the too violent action of the acid), an odour of acrolein is constantly evolved, and the substance becomes solid, of the consistence of plaster, resembles India-rubber, and no longer sticks to the fingers. It is then not completely fusible, dissolves to an emulsion in sulphide of carbon, shrinks when boiled with concentrated caustic potash, dissolves only on addition of water, and is again precipitated from the solution by acids. This substance is soluble in alcoholic potash and precipitable by acids; it swells in ether free from alcohol, and partly dissolves in a larger quantity of ether; alcohol precipitates it from the solution. In rock-oil it swells without dissolving; also in a little oil of turpentine, but dissolves completely in a larger quantity, and remains unaltered on evaporation. Linseed and nut oils yield eight or ten times as much of this caoutchouc-like substance as poppy oil (Jonas, N. Br. Arch. xlvi. 159; J. pr. Chem. xxxvii. 381).

Linseed oil submitted to *dry distillation* gives off, without boiling, white vapours, which condense to a colourless oil, having an odour of bread; on the disappearance of these vapours, it begins to boil, expands, and yields a distillate of brown empyreumatic products, until a mass resembling jelly and caoutchouc remains behind. (Sacc.)

Sulphur dissolves in hot linseed oil with red colour, partially crystallising on cooling; on longer heating, the oil takes up, with evolution of sulphydric acid, ¼th its weight of sulphur, and forms therewith a brown viscid mass: *fatty balsam of sulphur.* (See Radig, Horst and Ulex, N. Br. Arch. ii. 15; also Reinsch. J. pr. Chem. xlii. 136.) Linseed oil dissolves *selenium* (Berzelius); it dissolves nearly $\frac{1}{16}$th *arsenious acid*, whereby it is rendered heavier, precipitable by oil of vitriol and hydrochloric acid, and coagulable by alkalis (W. Henry, Schw. J. ii. 636). *Phosphorus* boiled with linseed oil acquires a scarlet colour (Reinsch. J. pr. Chem. xiv. 257). Heated with ¼th its weight of phosphorus to 75°, the oil becomes brown-black, and after cooling forms a leathery substance insoluble in linseed oil; ⅛th phosphorus forms a thin tar, which mixes with the drying oils. (Jonas, N. Br. Arch. lxx. 139.)

When linseed oil is heated with ⅓rd *iodine*, there pass over, first iodine, then an empyreumatic oil coloured brown by iodine; afterwards white vapours of hydriodic acid are evolved, followed by a thick yellowish oil, and at last charcoal, containing iodine, remains. (Reinsch. J. pr. Chem. xiv. 263.)

Brominated linseed oil is obtained by drenching the oil with 8 or 10 parts of water, heating it to between 50° and 80°, and adding bromine by drops as long as the colour disappears, removing the excess of bromine, if necessary, by further addition of oil. The product is then washed with warm water and dissolved in ether; the solution is shaken up with warm water, and the brominated oil thus freed is dried at 120°. It is brown, smells like linseed oil when heated, has a specific gravity of 1·345 at 14·5°, and contains 40·77 per cent. bromine, corresponding to the formula $C^{15}Br^2H^{26}O^2$. *Chlorinated linseed oil*, prepared in like manner, is a dark-yellow, thick liquid, of specific gravity 1·088 at 6·5°, and contains 22·62 per cent. chlorine ($C^{15}Cl^{12}H^{26}O^2$). (Lefort, J. Pharm. [3] xxiii. 343.)

On mixing from 15 to 25 pts. *chloride of sulphur* with 100 pts. linseed oil, caoutchouc-like products are obtained, which are the harder the more chloride of sulphur they contain, and are not attacked by moderately dilute acids and aqueous alkalis, but are ultimately saponified by concentrated alkalis. They become brown at 120°, and blacken and melt at a higher temperature. The addition of 5 per cent. chloride of sulphur thickens linseed oil, but does not cause it to harden; the product still retains the solubility of the fatty oils. When to a solution of 1 pt. linseed oil in 30 or 40 pts. sulphide of carbon, a quantity of chloride of sulphur is added equal to ¼th the weight of the oil, the mixture remains fluid for some days, and dries up to a varnish on wood. (Perra, Compt. rend. xlvii. 878; see also Compt. rend. xlvii. 972.)

With ⅛th its volume of syrupy *phosphoric acid*, linseed oil becomes brownish-yellow or green. (Calvert.)

Cold strong *sulphuric acid* colours it yellowish-brown (Gaultier de Claubry), dark red-brown (Heidenreich, van Kerckhoff); it coagulates the oil, colours it purple-red, violet, and black, and evolves sulphurous and formic acids; and there remains at last a tough, black, ropy, saponifiable mass (Sacc). From this last, water and alcohol take up substances which precipitate gelatin: *Hatchett's artificial tannin.* A mixture of 5 volumes linseed oil with 1 volume sulphuric acid of specific gravity 1·478 to 1·635, shaken vigorously, becomes green in 15 minutes (Calvert). When 15 grs. linseed oil are mixed with 7½ grs. sulphuric acid containing 90 per cent. H^2SO^4, the temperature rises to 75°. (Fehling, Dingl. pol. J. 129, 53.)

Linseed oil takes fire with fuming *nitric acid.* Linseed, hemp, and poppy oils take fire more easily than nut-oil; with dilute nitric acid an addition of sulphuric acid is necessary (Rouelle). A vigorously shaken mixture of linseed oil with ⅛th its volume of nitric acid of specific gravity 1·18 to 1·22, becomes yellow in 5 minutes; with acid of specific gravity 1·33, green to brown; with nitro-sulphuric (equal parts of oil of vitriol and nitric acid), green (Calvert, Phil. Mag. [4] vii. 101; J. pr. Chem. lxi. 354). See also Lescallier, J. Pharm. xiii. 203. Linseed oil shaken with water and very dilute nitric acid, is decolorised after some time, and converted into a varnish (Alm. 1782, 49). On dropping 2 to 4 drams of strong nitric acid into a hundredweight of hot linseed oil, a slimy sediment is formed, with frothing, and the oil is changed to a varnish, as with oxide of lead (Jonas, Ann. Ch. Pharm. xxxiv. 238).—A mixture of 1 pt. linseed oil, and 2 pts. commercial nitric acid, heated with 4 times its bulk of water, acquires a red colour, swells up, evolves nitric oxide, and forms a tough, elastic resin. This last contains margaric acid, and the mother-liquor oxalic and suberic acids. The resin, heated with nitric acid, again becomes oily, and is then decomposed (the margaric acid only remaining), with formation of suberic and pimelic acids and a volatile fatty substance having the odour of butyric acid (Sacc).—With *nitrous acid* linseed oil does not form elaidic acid. (Pelouze and Boudet.)

In contact with aqueous *ammonia* and alcohol, it is attacked with difficulty, and yields a small quantity of warty crystals of an amide which melts at 100°, solidifies at 97°, and dissolves easily in alcohol; it contains, on an average, 75·25 per cent. C, 13·02 H, and 5·03 N, and has therefore the composition of margaramide, with which it is identical. (Rowney, J. pr. Chem. lxvii. 159.)

Linseed oil yields, with *alkalis*, a very soft soap. On heating with $\frac{1}{5}$th its volume of caustic soda of specific gravity 1·34, it turns yellow and remains fluid (Calvert). By distillation with an excess of alkali, it evolves hydrogen, together with a fishy odour, and yields a green distillate. (Al. Müller, *Handwörterb.*, vi. 874.)

Potassium and *sodium* oxidise in linseed oil somewhat more quickly than in volatile oils, with formation of soap. (Gay-Lussac and Thénard.)

Linseed oil is oxidised with peculiar facility by *acid chromate of potassium* and dilute sulphuric acid, and yields an acid, strongly-smelling distillate. (Arzbächer, Ann. Ch. Pharm. lxxiii. 199.)

It dissolves oxide of lead when heated, and is decolorised thereby and rendered more easily drying, forming what is called *boiled oil* (see Liebig, Ann. Ch. Pharm. xxxiii. 110; W. Henry, Scher. J. ii. 636; Schindler, N. Br. Arch. xli. 146; Varrentrapp *Handwörterb.* iii. 123). When shaken with *basic acetate of lead* and left at rest, it throws down a turbid mucus containing oxide of lead, above which is a yellow varnish containing 4 or 5 per cent. oxide of lead. Exposed to the sun in contact with *mercuric oxide*, it reduces the mercury to a liquid mass (Fuchs, Ann. Ch. Pharm. xx. 200); partial reduction takes place in strong sunshine, the oxide becoming blackish-grey; but it is only when heat is applied, that a small quantity of metal is obtained. (Ann. Ch. Pharm. xx. 200.)

Linseed oil dissolves, according to Bucholz, in about 5 pts. of boiling and 40 pts. of cold alcohol; according to Brandes (Gilb. Ann. xliv. 289), in 32 pts. alcohol of specific gravity 0·82 and in 1·6 pt. ether.

LIPARITE. Syn. with FLUOR SPAR (ii. 677).

LIPIC ACID. $C^5H^6O^5 = C^5H^4O^4 . H^2O$ according to Laurent (Ann. Ch. Phys. lxvi. 169); $C^5H^8O^4$ according to Wirz (Ann. Ch. Pharm. cv. 257); the latter formula places it among the homologues of oxalic acid, included in the general formula $C^nH^{2n-2}O^4$. This acid, discovered by Laurent, is produced, together with pimelic, suberic, adipic, and other acids, by the action of nitric acid upon oleic, stearic, or palmitic acid, and is contained in the mother-liquor which remains after the pimelic and suberic acids have been separated.

The best mode of preparing it, is to heat oleic acid in a retort for about 12 hours with an equal weight of nitric acid of ordinary strength, then add fresh nitric acid, and repeat the operation four or five times. The united solutions are then to be evaporated to a fourth of their bulk, and the concentrated liquid left at rest, till pimelic and suberic acids crystallise out. The remainder of the nitric acid must then be removed from the mother-liquor by evaporation as completely as possible, taking care that the mass does not blacken from too great concentration; the crystals which separate from it, consisting of adipic and lipic acids, are dried and dissolved in hot ether, which leaves a few brown impurities undissolved; the solution is left to evaporate to half its bulk, and the liquid which covers the crystals is evaporated. The two products thus obtained by evaporating the ether are separately dissolved in boiling alcohol, and the solutions are left to evaporate in the air. By repeating these operations several times, two acids are obtained, viz. adipic acid crystallised in rounded tuberculous aggregated grains, and lipic acid in slightly elongated laminæ (Laurent), in translucent crusts made up of nodular groups of small prisms. (Wirz.)

Lipic acid is moderately soluble in cold *water*. When a few grains of it are heated on a watch-glass, till partial fusion takes place, the acid crystallises on cooling in a fibrous mass, while a portion volatilises and condenses on the non-melted mass in beautiful needles having the form of prisms with rectangular base.

The acid crystallised from water, contains 1 at. water, which it loses by sublimation, the anhydrous acid then condensing in long shining needles (Wirz). Its vapour is very suffocating and excites coughing. When deprived of its water of crystallisation, it does not melt below 140° or 145° (Laurent); according to Wirz it melts at 150°. It is very soluble in *alcohol* and *ether*.

Lipic acid is dibasic, the formula of its salts being $C^5H^4M^2O^4$, which is the same as that of the itaconates (Laurent); $C^5H^6M^2O^4$ (Wirz). The salts when heated with sulphuric acid give off lipic acid.

The *ammonium-salt* crystallises in long prisms (Laurent).—The *barium-salt* separates after a while from a mixed solution of chloride of barium and lipate of ammonium in quadratic prisms, passing into the octahedron (Laurent).—The *calcium-salt* is precipitated in like manner in square-based prisms, containing, according to Wirz, $C^5H^6Ca^2O^4.H^2O$.—The *cupric salt*, $C^5H^6Cu^2O^4$, is obtained, by boiling cupric carbonate with the acid, in green crystalline scales, which may be freed from adhering acid by heating to 150°—200° (Wirz).—The *silver-salt* contains $C^5H^4Ag^2O^4$ (Laurent); $C^5H^6Ag^2O^4$ (Wirz).—The *sodium-salt* crystallises in flat rhombic prisms containing $C^5H^6Na^2O^4.6H^2O$. (Wirz.)

The existence of lipic acid must, however, be regarded as somewhat doubtful. Gerhardt regarded it merely as impure succinic acid, and Arppe (Ann. Ch. Pharm. cxv. 143) in his more recent investigation of the products of the action of nitric acid on oleic acid, has arrived at the same conclusion. He prepared the acids by Laurent's process above described, from oleic acid obtained by saponification of the so-called stearin-oil. The yellow solution obtained by evaporating the nitric acid with addition of water, yielded a granular powder, which, after repeated crystallisation, melted at 127°, and was found to consist of suberic acid mixed with another acid which could be extracted by cold ether, and proved to be azelaic acid (p. 572); the same acid was also found in the mother-liquors of the suberic acid.

LIPYL. A hypothetical radicle, C^3H^4, supposed by Berzelius to exist in the natural fats and fatty acids. At present however these compounds are regarded as derivatives of the triatomic radical *glyceryl*, C^3H^5. (See ETHERS, ii. 519, and GLYCERIDES, ii. 877.)

LIQUID. This term is applied to bodies in that peculiar state of aggregation, intermediate between the solid and the gaseous, in which the particles are free to move amongst themselves in all directions, but do not exhibit the constant tendency to fly asunder which is characteristic of the gaseous state.* The conditions which are supposed to give rise to this particular state of aggregation have been already considered in connection with the dynamical theory of heat (p. 133).

LIQUIDAMBAR. A balsam produced from a large tree (*Liquidambar styraciflua*) growing in Lousiana, Florida, and Mexico.

Liquid liquidambar, or *Oil of liquidambar*, which is obtained by making incisions in the tree, is received immediately in vessels to protect it from the air, and decanted after a while to separate a portion of the opaque balsam which settles to the bottom. It has the consistence of a thick oil, is transparent, of amber-yellow colour, and has an odour like that of liquid storax, but more agreeable; its taste is aromatic and irritates the throat. It contains a considerable quantity of benzoic or cinnamic acid, and a drop of it reddens litmus strongly. Treated with boiling alcohol, it leaves only a small residue, and the filtered liquid becomes turbid on cooling.

Soft or *White Liquidambar* proceeds either from the opaque deposit above mentioned, or from parts of the balsam which have run down the stem of the tree, and thickened by exposure to the air. It has the consistence of very thick turpentine or soft pitch; it is opaque and whitish; its odour is less strong and more agreeable than that of the oil just mentioned; taste, sweet and aromatic, but irritating. It contains a large quantity of benzoic or cinnamic acid. By long exposure to the air it solidifies completely and becomes almost transparent. It was formerly sold under the name of *White Peru balsam*. (Gerh., iv. 386.)

LIQUIDS, DIFFUSION OF. When two liquids of different density, and capable of mixing, are placed in contact, diffusion takes place between them, much in the same manner as between gases, excepting that, as the particles of the liquid are less freely mobile than those of the gas, the rate of diffusion is slower. The phenomena of liquid diffusion have been minutely investigated by Graham, in two classical series of researches published in the Philosophical Transactions for 1850 and 1862, also in the Journal of the Chemical Society, iii. 60, 257; iv. 83, and xv. 216; and important contributions to the subject have also been made by Fick, Simmler and Wilde, Beilstein and others.

The rate of diffusion varies with the nature of the liquids, the temperature, and in the case of solutions, with the degree of concentration.

1. **Diffusion of Saline Solutions.** The apparatus used in Graham's first series of experiments consisted of a set of phials of nearly equal capacity, cast in the same mould, and further adjusted by grinding to a uniform size of aperture. The phials were 3·8 inches high, with a neck 0·5 inch in depth, and aperture 1·25 inch wide; capacity to base of neck equal to 2080 grains of water or between 4 and 5 ounces. For each *diffusion-phial* a plain glass water-jar was also provided 4 inches in diameter and 7 inches deep. (*Fig.* 708.)

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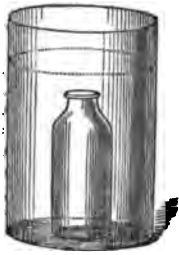
* Many writers use the term "fluid" as synonymous with liquid; but this is incorrect; *fluid* is, properly speaking, the correlative of *solid*, and includes both liquid and gas.

The diffusion-phial was filled with the saline solution, sal-ammoniac for instance, to the base of the neck, or more correctly to a distance of 0·5 inch from the ground surface of the lip. The neck of the phial was then filled up with distilled water, a light float being first placed on the surface of the solution, and care being taken to avoid agitation. After the phial had been placed within the jar, water was poured into the jar, so as to cover the open phial to the depth of an inch, which required about 20 ounces of water. The saline liquid in the phial is thus allowed to communicate freely with the water in the jar. The diffusion is interrupted by placing a small plate of ground glass on the mouth of the phial, and raising the latter out of the jar. The amount of salt diffused, called the diffusion-product, or diffusate, is ascertained by evaporating the water in the jar to dryness, or, in the case of chlorides, by precipitating with nitrate of silver.

Fig. 708.



The results of several series of experiments made in this manner are given in the following table, the second column of which gives the quantity of salt in 100 pts. of the solution, one per cent. of salt amounting to 20·8 grains; the third, the time of diffusion; the fourth, the temperature, on the Fahrenheit scale; the fifth, the quantity of salt diffused in grains:—

TABLE I.—DIFFUSION OF SALINE SOLUTIONS.

Substance.	Per cent.	Days.	Fahr.	Diffusate.
Hydrochloric acid . . .	1	5	51 °	7·41
	2	5	51·0	15·04
	2	5	59·7	16·55
	4	5	51·0	30·72
	8	5	51·0	67·68
Hydriodic acid . . .	2	5	51·0	15·11
Hydrobromic acid . . .	2	. .	59·7	16·58
Bromine	0·864	10	60·1	5·84
Hydrocyanic acid . . .	1·766	5	64·2	11·68
Hydrated nitric acid (NO^6H) .	1	5	51·2	6·99
	2	5	51·2	14·74
	4	5	51·2	28·76
	8	5	51·2	57·92
Hydrated sulphuric acid (SO^4H)	1	10	49·7	8·69
	2	10	49·7	16·91
	4	10	49·7	33·89
	8	10	49·7	68·96
Chromic acid . . .	1·762	10	67·3	19·78
Acetic acid ($C^4H^4O^4$) . .	2	10	48·8	11·31
	4	10	48·8	22·02
	8	10	48·8	41·80
Sulphurous acid . . .	1	10	68·1	8·09
	2	10	68·1	16·96
	4	10	68·1	33·00
	8	10	68·1	66·38
Ammonia	1	4·04	63·4	4·93
	2	4·04	63·4	9·59
	4	4·04	63·4	19·72
	8	4·04	63·4	41·22
Alcohol	2	10	48·7	8·62
	4	10	48·7	16·12
	8	10	48·7	35·50
Nitrate of barium . . .	1	11·43	64·1	7·72
	2	11·43	64·1	15·04
	4	11·43	64·1	29·60
	8	11·43	64·1	54·50
Nitrate of strontium . .	0·82	11·43	51·5	5·59
Nitrate of calcium . . .	1	11·43	64·1	7·66
	2	11·43	64·1	15·01
	4	11·43	64·1	29·04
	8	11·43	64·1	55·10
Acetate of barium . . .	1	16·17	53·5	7·50

TABLE I.—*continued.*

Substance.	Per cent.	Days.	Fahr.	Diffusate.
Acetate of lead . . .	1	16·17	53·1°	7·84
Chloride of barium . .	1	8·57	63·0	6·32
	2	8·57	63·0	12·07
	4	8·57	63·0	23·96
	8	8·57	63·0	45·92
Chloride of strontium . .	1	8·57	63·0	6·09
	2	8·57	63·0	11·66
	4	8·57	63·0	23·56
	8	8·57	63·0	44·46
Chloride of calcium . .	1	11·43	63·8	7·92
	2	11·43	63·8	15·35
	4	11·43	63·8	30·78
	8	11·43	63·8	61·56
	1	11·43	50·8	6·51
Chloride of manganese . .	1	11·43	50·8	6·63
Nitrate of magnesium . .	1	11·43	50·8	6·49
Nitrate of copper . . .	1	11·43	50·8	6·44
Chloride of zinc . . .	1	11·43	50·8	6·29
Chloride of magnesium . .	1	11·43	50·8	6·17
Cupric chloride . . .	1	11·43	50·8	6·06
Ferrous chloride . . .	1	11·43	53·5	6·30
Sulphate of magnesium . .	1	16·17	65·4	7·31
	2	16·17	65·4	12·79
	4	16·17	65·4	23·46
	8	16·17	65·4	42·82
	8	16·17	62·8	42·66
	16	16·17	62·8	75·06
	24	16·17	62·8	102·04
Sulphate of zinc . . .	1	16·17	65·4	6·67
	2	16·17	65·4	12·22
	4	16·17	65·4	23·12
	8	16·17	65·4	42·26
	8	16·17	62·8	39·62
	16	16·17	62·8	74·40
	24	16·17	62·8	101·42
Sulphate of aluminium . .	1	16·17	65·4	5·48
	2	16·17	65·4	10·21
	4	16·17	65·4	19·28
	8	16·17	65·4	33·52
Nitrate of silver . . .	2	7	63·4	13·61
	4	7	63·4	26·34
	8	7	63·4	51·88
Nitrate of sodium . . .	2	7	63·4	12·35
	4	7	63·4	23·56
	8	7	63·4	47·74
Chloride of sodium . .	1	7	63·4	6·32
	2	7	63·4	12·37
	4	7	63·4	24·96
	8	7	63·4	48·44
	2	7	63·4	12·14
Iodide of sodium . . .	2	7	59·8	12·18
Bromide of sodium . .	2	7	59·8	12·14
Chloride of potassium . .	2	5·716	59·8	12·24
Bromide of potassium . .	2	5·716	59·8	12·46
Iodide of potassium . .	2	5·716	59·8	12·51
Chloride of ammonium . .	1	5·716	59·8	5·99
Bicarbonate of potassium .	1	8·08	68·2	7·23
	2	8·08	68·2	14·05
	4	8·08	68·2	26·72
	8	8·08	68·2	52·01
Bicarbonate of ammonium .	1	8·08	68·2	6·91
	2	8·08	68·2	13·65

TABLE I.—*continued.*

Substance.	Per cent.	Days.	Fahr.	Diffusate.
Bicarbonate of ammonium	4	9·87	68·2°	27·00
	8	9·87	68·2	50·10
Bicarbonate of sodium	1	9·87	68·2	7·31
	2	9·87	68·2	13·81
	4	9·87	68·2	26·70
	8	9·87	68·2	52·38
Hydrate of potassium	1	4·04	63·3	6·56
	2	4·04	63·3	12·84
	4	4·04	63·3	25·04
	8	4·04	63·3	52·24
Hydrate of sodium	1	4·95	63·2	5·81
	2	4·95	63·2	11·09
	4	4·95	63·2	20·86
	8	4·95	68·2	40·44
Carbonate of potassium	1	8·08	68 6	6·13
	2	8·08	63·6	11·92
	4	8·08	63·6	22·88
	8	8·08	63·6	45·44
Carbonate of sodium	1	9·9	63·4	6·02
	2	9·9	63·4	11·70
	4	9·9	63·4	21·42
	8	9·9	63·4	39·74
Sulphate of potassium	1	8·08	60·2	6·16
	2	8·08	60·2	11·60
	4	8·08	60·2	22·70
	8	8·08	60·2	43·92
Sulphate of sodium	1	9·9	59·9	6·33
	2	9·9	59·9	12·00
	4	9·9	59·9	21·96
	8	9·9	59·9	41·38
Sulphite of potassium	2	8·08	59·5	11·63
Sulphite of sodium	2	9·9	59·5	11·83
Hyposulphite of potassium	2	8·08	59·7	12·37
Hyposulphite of sodium	2	9·9	59·9	11·89
Sulphovinate of potassium	2	8·08	59·7	12·60
Sulphovinate of sodium	2	9·9	59·5	13·03
Oxalate of potassium	1	8·08	59·9	6·20
	2	8·08	59·9	12·17
	4	8·08	59·9	2·4
	8	8·08	59·9	42·82
Oxalate of sodium	1	9·9	59·9	6·24
Acetate of potassium	1	8·08	60·2	6·44
	2	8·08	60·2	12·52
	4	8·08	60·2	23·44
	8	8·08	60·2	47·26
Acetate of sodium	1	9·9	59·5	6·67
	2	9·9	59·5	12·46
	4	9·9	59·5	25·04
	8	9·9	59·5	48·04
Tartrate of potassium	2	8·08	59·9	10·96
Tartrate of sodium	2	9·9	59·5	10·65
Hydrochlorate of morphine	2	11·43	64·1	11·60
Hydrochlorate of strychnine	2	11·43	64·1	11·49

These experiments, and a number of others made in a similar manner, lead to the following general conclusions:

1. Different salts, in solutions of equal strength, diffuse unequally in equal times.

2. With each salt, the rate of diffusion increases with the temperature, and at any given temperature, is proportionate to the strength of the solution, at least when the quantity of salt dissolved does not exceed 4 or 5 per cent.

Later experiments (Chem. Soc. J. xv. 235) have shown that diffusion increases at a higher, though not greatly higher, rate than the temperature, and that the more highly diffusive the substance, the less does it gain in diffusiveness by rate of temperature. For hydrochloric acid the rate of diffusion was found to increase as follows:

Diffusion at 15·55 C. (60° F.) = 1
" 26·66 C. (80° F.) = 1·3545
" 37·77 C. (100° F.) = 1·7732
" 41·88 C. (120° F.) = 2·1812

3. There exist classes of equidiffusive substances which coincide in many cases with the isomorphous groups, but are, on the whole, more comprehensive than the latter. Thus, the same rate of diffusion is exhibited by hydrochloric, hydrobromic, and hydriodic acid; by the chlorides, iodides, and bromides of the alkali-metals; by the nitrates of barium, strontium, and calcium; the sulphates of magnesium and zinc, &c. &c.

4. For several groups of salts, it is found that the squares of the times of equal diffusion, from solutions of the same strength, stand to one another in a simple numerical relation. Thus, the diffusate from a solution of nitrate of potassium in 7 days, was equal to that obtained from an equally strong solution of carbonate of potassium, in 9·9 days, numbers which are to one another as $1 : \sqrt{2} = 1·414$. Similar results were obtained with 2 per cent. solutions of nitrate and sulphate of potassium, equal diffusates of the two being obtained in 3·5 and 4·95 days, in 7 and 9·9 days, and in 10·5 and 14·85 days; also, with hydrate and nitrate of potassium, and with nitrate and carbonate of sodium. The times of equal diffusion of 1 per cent. solutions of chloride of ammonium and chloride of sodium, were to one another as $\sqrt{2} : \sqrt{3}$. Now, according to Graham's experiments (ii. 812), the squares of the times of equal diffusion of gases are to one another in the ratio of their densities. Hence, by analogy, it may be inferred that the molecules of these several salts, as they exist in solution, possess densities which are to one another as the squares of the times of equal diffusion. Thus the *solution-densities* of sulphate, nitrate, and hydrate of potassium, are to one another as the squares of the numbers 4, 2 and 1, that is as 16, 4 and 1. These solution-densities appear to relate to a kind of molecules different from the chemical atoms, and the weights of which are either equal, or bear to one another a simple numerical relation.

The diffusion of a salt into the solution of another salt takes place with nearly the same velocity as into pure water; at least, when the solutions are dilute. Graham has shown that the diffusion of a 4 per cent. solution of carbonate of sodium, is not sensibly affected by the presence of 4 per cent. of sulphate of sodium in the liquid atmosphere; nor that of a 4 per cent. solution of nitrate of potassium, by the same proportion of nitrate of ammonium. The presence of 4 per cent. of sulphate of sodium reduced the diffusion of carbonate of sodium by only $\frac{1}{8}$ of the whole. In stronger solutions the retardation would probably be greater. There is, indeed, reason to believe that the phenomena of liquid diffusion are exhibited in their simplest form only by weak solutions, the effect of concentration, like that of compression in gases, being to produce a departure from the normal character.

The rate of diffusion is, however, materially affected when the liquid atmosphere already contains a portion of the diffusing salt. The consideration of this case leads to the general question of the motion of particles of a dissolved substance in a solution of unequal concentration. The general law which regulates such movements appears to be this:—*The velocity with which a soluble salt diffuses from a stronger into a weaker solution, is proportioned to the difference of concentration between two contiguous strata.* This law has not yet been experimentally demonstrated in a sufficient number of cases to establish it completely; but in the case of chloride of sodium, it has been shown to be true by the following experiments of Fick. (Phil. Mag. [4] x. 30.)

A cylindrical glass tube, open at both ends, was cemented into a vessel completely filled with common salt, the cylindrical space filled up with water, and the whole immersed in a large jar containing water. The apparatus was then left to itself for several weeks, the water in the jar being from time to time taken out and renewed. Now, as the lowest stratum of liquid in the tube, being in contact with undissolved salt, must remain constantly saturated, while the uppermost layer, which is in contact with pure water, contains no salt at all, a certain normal state of diffusion will ultimately establish itself throughout the length of the tube, characterised by the condition, that each horizontal stratum will, in a given time, give up to the stratum immediately above it as much salt as it receives from the one below. When this state is attained, the densities of the successive strata decrease from below upwards in arithmetical progression. This law of decrease was verified experimentally by immersing in the liquid, at various depths, a glass bulb suspended from the arm of a balance, and counterpoised by weights in the opposite scale. This law of decrease, however, is true only with regard to cylindrical columns of liquid, or others, in which the horizontal section is of uniform magnitude. In other cases, the law of decrease of density may be calculated according to the form of the vertical section. In funnel-shaped tubes Fick has shown that the results of calculation agree with those of experiment.

Now let K denote the quantity of salt which, in the normal state of diffusion, passes, in a unit of time, through a unit of horizontal section of a cylindrical tube whose height is equal to the unit of length; this quantity is called the *diffusion-coefficient;* also, let Q be the quantity of salt which, in the time t, flows from the mouth of the tube into the water-atmosphere; h, the height of the tube; s, its horizontal section; and d, the density of the liquid at the bottom; then

$$Q = K . d . \frac{h}{s} t.$$

Hence, with a tube of given dimensions, and a solution of known and constant density at the bottom, the *diffusion-coefficient* K, of any salt may be calculated from the quantity Q, diffused out in a given time.

This method has been applied by Fick only in the case of chloride of sodium. It is, in fact, though simple in principle, somewhat inconvenient of application, on account of the long time—at least fourteen days—which must elapse before the normal state is attained.

Another method of determining the diffusion-coefficient of a salt has been devised by Jolly, and applied in several cases by Beilstein (Ann. Ch. Pharm. xcix. 165). The apparatus used consists of a glass tube (*fig.* 709), about three inches long, bent round at the bottom, and cut off near the bend, so that the level of the orifice is not much more than a millimetre above the bottom of the bend. The upper end of the tube is slightly drawn out and closed with a stopper. This tube is filled with a solution of known concentration, and fixed upright within a jar of water, the orifice of the tube being two or three lines below the level of the water. The salt then immediately begins to diffuse into the water, and as the liquid near the orifice becomes diluted, it passes round the bend to the upper part of the tube, its place being supplied by more concentrated liquid from above. With this apparatus, Beilstein has obtained the following diffusion-coefficients (taking that of chloride of potassium for unity), for solutions containing 4 per cent. of salt, and at the temperature of 6° C. (42·8° F.)

Fig. 709.

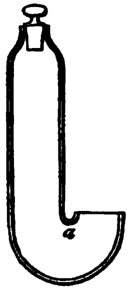


TABLE II.—*Diffusion-coefficients.*

Chloride of potassium	1·0000	Sulphate of potassium	0·6987
Nitrate of potassium	0·9487	Carbonate of sodium	0·5436
Chloride of sodium	0·8337	Sulphate of sodium	0·5369
Bichromate of potassium	0·7543	Sulphate of magnesium	0·3587
Carbonate of potassium	0·7371	Sulphate of copper	0·3440

Beilstein infers from his experiments, that the rate of diffusion is not exactly proportional to the difference of density of two contiguous strata, but increases in a somewhat greater ratio.

Simmler and Wilde (Pogg. Ann. c. 217) are of opinion that the want of agreement of Beilstein's results with this law arises from a defect in the method of experimenting. Beilstein's calculations, indeed, are based on the supposition that the strength of the solution in the tube (*fig.* 709), though constantly decreasing, is uniform at any instant of time throughout the entire length; whereas, a little consideration will show that the density near the orifice must be less than that in the larger arm of the tube, and in this arm less than near the bottom of the bend, where the liquid must stagnate to a certain extent. From this source of error, Fick's mode of observation is free. Simmler and Wilde, however, propose other methods, easier of execution than Fick's, and not subject to the necessity of waiting till the normal state of diffusion is established. One of these methods is similar to that adopted by Graham (p. 706), excepting that the vessel containing the solution is perfectly cylindrical, a condition which greatly simplifies the calculations; and, instead of being placed at the bottom of the water-jar, is supported on a stand, so as to bring its mouth within a line or two below the surface of the water; the salt, as it diffuses out, is thus made to flow over the sides of the vessel and fall to the bottom, leaving an atmosphere of pure water above. Another method proposed by the same authors is to place the saline solution in a vessel having the form of a triangular prism, and determine the variation of density at different depths below the surface by observation of the indices of refraction.

Graham, in his later experiments (Phil. Trans. 1862, part i.; Chem. Soc. J. xv. p. 217) also uses a plain glass jar, in which the salt is allowed to rise from below in a cylindrical column. The jars were 152 mm. (6 inches) in height, and 87 mm. (3·45 inches) in width. In operating, seven-tenths of a litre of water were first placed in the jar, and then one-tenth of a litre of the liquid to be diffused was carefully conveyed to the bottom of the jar by means of a fine pipette. The whole fluid column then measured 127 mm. (5 inches) in height. As much as five or six minutes of time were occupied in emptying the pipette at the bottom of the jar, and extremely little disturbance was occasioned in the superincumbent water, as could be distinctly seen when the liquid introduced by the pipette was coloured. The jar was then left undisturbed, to allow diffusion to proceed, the experiments being always conducted in an apartment of constant, or nearly constant temperature. When a certain time had elapsed, the diffusion was interrupted by drawing off the liquid from the top by means of a small siphon, slowly and deliberately, as the liquid had been first introduced, in portions of 50 cubic centimetres, or one-sixteenth of the whole volume. The open end of the short limb of the siphon was kept in contact with the surface of the liquid in the jar, and the portion of liquid drawn off was received in a graduated measure. By evaporating each fraction separately, the quantity of salt which had risen into equal sections of the liquid column was ascertained. A particular advantage of this method is that it affords the means of ascertaining the absolute rate or velocity of diffusion, rendering it possible to state the distance which a salt travels per second in terms of the meter. Such a constant must enter into all the chronic phenomena of physiology, and holds a place in vital science not unlike the time of the falling of heavy bodies in the physics of gravitation.

2.—Crystalloïds and Colloïds.

The substances whose diffusion has been considered in the preceding pages, though they exhibit considerable diversities in their diffusive mobility, all belong to the more diffusive class. Opposed to them is another class, which are much less diffusive, and are likewise distinguished from the former by several well-defined physical and chemical characters, especially by the absence of the power to crystallise. Such are hydrated silicic acid, hydrated alumina, and other metallic oxides of the aluminous class, when they exist in the soluble form; also starch, dextrin and the gums, caramel, tannin, albumin, gelatin, vegetable and animal extractive matters. These bodies are also distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation, together with the chemical indifference referred to, appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, substances of this class may be designated as *colloïds* (from κόλλα, glue), and their peculiar form of aggregation, as the *colloïdal condition of matter*. Opposed to the colloïdal is the crystalline condition. Substances affecting the latter form may be classed as *crystalloïds*. The distinction is no doubt one of intimate molecular constitution.

Although chemically inert in the ordinary sense, colloïds possess a compensating activity of their own, arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloïd partakes of fluidity, and enables the colloïd to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloïds as can exist at a high temperature. Hence a wide sensibility on the part of colloïds to external agents. Another and eminently characteristic quality of colloïds, is their mutability. Their existence is a continued metastasis. A colloïd may be compared in this respect to water while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloïds appear to have always a *pectous* modification; and they often pass, under the slightest influences, from the first into the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinise and become insoluble at last. Nor does the change of this colloïd appear to stop at that point. For the mineral forms of silicic acid, deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloïdal into the crystalline condition (H. Rose). The colloïdal is, in fact, a dynamical state of matter; the crystalloïdal being the statical condition. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloïdal changes take place (for they always demand time as an element), may the characteristic protraction of chemico-organic changes also be referred.

The following experiments made by the method of jar-diffusion (p. 700), exhibit the difference of diffusibility of colloïds, namely gum, tannin, or caramel, as compared with the crystalloïdal substances, chloride of sodium, sulphate of magnesium, and cane-sugar.

TABLE III.—*Diffusion of* 10 *per cent. solutions* (10 *grms. of substance in* 100 *cubic centimetres of liquid*) *into pure water, after fourteen days, at* 10° (50 *Fahr.*)

Number of stratum (from above downwards).	Chloride of sodium.	Sulphate of magnesium, at 10°.	Sugar.	Gum.	Tannin.	Albumin at 13°—13° 5.	Caramel at 10°—11°.
1	·104	·007	·005	·003	·003		
2	·129	·011	·008	·003	·003		
3	·162	·018	·012	·003	·004		
4	·198	·027	·016	·004	·003		
5	·267	·049	·030	·003	·005		
6	·340	·085	·059	·004	·007	. .	·003
7	·429	·133	·102	·006	·017	. .	·005
8	·535	·218	·180	·031	·031	·010	·010
9	·654	·331	·305	·097	·069	·015	·023
10	·766	·499	·495	·215	·145	·047	·033
11	·881	·730	·740	·407	·288	·113	·075
12	·991	1·022	1·075	·734	·556	·343	·215
13	1·090	1·383	1·435	1·157	1·050	·855	·705
14	1·187	1·803	1·758	1·731	1·719	1·892	1·725
15 and 16	2·266	3·684	3·783	5·601	6·097	6·725	7·206
	9·999	10·000	10·003	9·999	9·997	10·000	10·000

Here the superimposed column of water being 111 millimetres (4·38 inches) high, the chloride of sodium is found to have diffused in sensible quantity to the top, and could have risen higher. The top of the diffusion-column of sulphate of magnesium, and likewise that of sugar, appear to have just reached the top of the liquid in the fourteen days of the experiment. But the colloïds, gum, tannin, albumin and caramel, exhibit a great falling off in the rate of diffusion. Gum and tannin do not appear to be carried by diffusion higher than the seventh stratum, the minute quantities found in the higher strata, which together do not exceed 0·02 grm., being doubtless the result of accidental dispersion, arising probably from a movement of the upper liquid, occasioned by slight inequalities of temperature. The diffusion of albumin and of caramel is still slower.

By continuing the diffusion of different substances till equal quantities had diffused out, the following results were obtained:

Approximate times of Equal Diffusion.

Hydrochloric acid	1
Chloride of sodium	2·33
Sugar	7
Sulphate of magnesium	7
Albumin	49
Caramel	98

The diffusion of hydrochloric acid in three days corresponds with the diffusion of chloride of sodium in seven days. Hydrochloric and the allied hydracids, with other monobasic acids, are the most diffusive substances known.

The diffusion process in alcohol appears to be several times slower than in water. The following table exhibits the results of experiments on three substances dissolved in alcohol, and placed under a column of alcohol, the experiments being conducted exactly as described at p. 700.

TABLE IV.—*Diffusion of* 10 *per cent. solutions of Iodine and Acetate of Potassium in alcohol in seven days.*

Number of stratum.	Iodine at 14°.	Acetate of potassium at 14°—15°.	Resin at 14·5°.
1	·028	·055	·017
2	·033	·057	·017
3	·046	·061	·018
4	·038	·063	·017
5	·037	·064	·019
6	·039	·066	·020
7	·081	·070	·022
8	·143	·071	·024
9	·263	·072	·025
10	·417	·095	·080
11	·637	·285	·210
12	·936	·619	·498
13	1·235	1·157	·992
14	1·506	1·907	1·700
15 and 16	4·561	5·358	6·341
	10·000	10·000	10·000

3.—Application of Liquid Diffusion to Chemical Analysis.

Mixed salts may be more or less separated by their unequal diffusibility. A solution of 1 pt. of carbonate of potassium, and 1 pt. carbonate of sodium in 10 pts. of water placed in a a diffusion-phial (*fig.* 708), yielded in 10 days at 15° a diffusate containing 63·6 pts. carbonate of potassium to 36·4 pts. carbonate of sodium; the diffusate in 25 days contained the same salts in nearly the same proportion. Inequality of diffusion is indeed somewhat increased by mixture, so that the actual separation is greater than that calculated from the relative diffusibilities of the mixed substances.

Similar results were obtained by the method of jar-diffusion at p. 700; when a mixture of two salts was placed at the bottom of the jar, the more diffusive salt travelled upwards the most rapidly, showing itself first, and always most largely, in the upper strata. The following table shows the results obtained with a mixture of equal parts of the chlorides of potassium and sodium.

TABLE V.—*Diffusion of a mixture of 5 per cent. of Chloride of Potassium, and 5 per cent. of Chloride of Sodium, for seven days at* 12°—13°.

Number of stratum.	Chloride of potassium.	Chloride of sodium.	Total Diffusate.
1	·018	·014	·032
2	·025	·015	·040
3	·044	·014	·058
4	·075	·017	·092
5	·101	·034	·135
6	·141	·063	·204
7	·185	·104	·289
8	·252	·151	·403
9	·330	·212	·542
10	·349	·351	·700
11	·418	·458	·876
12	·511	·559	1·070
13	·552	·684	1·236
14	·615	·772	1·387
15 and 16	1·385	1·551	2·936
	5·001	4·999	10·000

The first six strata contain together 561 milligrammes, of which 404 milligrammes, or 72 per cent., that is nearly three-fourths, are chloride of potassium. We have to descend to the tenth stratum before the salts are found in equal proportions. The progression is then inverted, and chloride of sodium comes to preponderate in the lower strata.

It is evident that the preceding experiment might be so conducted as to diffuse away the chloride of potassium, and leave below a mixture containing chloride of sodium in relative excess, to as great an extent as the chloride of potassium is found above, in the last experiment.

Further, the mixture in which chloride of potassium was concentrated in the experiment described, so as to form 72 per cent. of the whole mixture, might be again subjected to diffusion in the same manner. In an experiment upon a mixture of 7·5 grms. of chloride of potassium and 2·5 grms. of chloride of sodium, the six upper strata gave 640 milligrms. of salt, of which 610 milligrms., or 95·3 per cent., were chloride of potassium. It is obvious that, by repeating this diffusive rectification a sufficient number of times, a portion of the more diffusive salt might be obtained at last in a state of sensible purity.

The preceding example illustrates the separation of unequally diffusive metals or bases; the following example represents, on the other hand, the separation of unequally diffusive acids united with a common base. Chloride and sulphate of sodium diffuse separately in the phial experiments in the proportion of 1 to 0·707.

TABLE VI.—*Diffusion of 5 per cent. of Chloride of Sodium and 5 per cent. of anhydrous Sulphate of Sodium, for 7 days, at 10°—10°·75.*

Number of stratum.	Chloride of sodium in grammes.	Sulphate of sodium in grammes.	Total diffusate in grammes.
1	·009	. .	·009
2	·012	·001	·014
3	·024	·005	·026
4	·038	·003	·041
5	·060	·006	·066
6	·095	·012	·107
7	·141	·029	·170
8	·203	·059	·262
9	·278	·115	·393
10	·360	·205	·565
11	·473	·317	·790
12	·560	·507	1·067
13	·637	·694	1·331
14	·713	·909	1·627
15 and 16	1·390	2·141	3·531
	4·999	5·000	9·999

Here the separation is still more sensible than with the bases. The six upper strata contain 263 milligrammes of salt, of which 239 milligrammes, that is 90·8 per cent., are chloride of sodium. The salt of the upper eight strata amounts to 695 milligrammes, of which 583 milligrammes, or 83·9 per cent., are chloride.

On comparing the diffusion of a mixture of equivalent quantities of chloride of sodium and sulphate of potassium with that of a mixture, also in equivalent proportions, of chloride of potassium and sulphate of sodium, it was found that the diffusion of the metals is not affected by the acid with which each of them is originally combined. This result is quite in harmony with Berthelot's view, that the acids and bases are indifferently combined, or that a mixture of chloride of potassium and sulphate of sodium is the same thing as a mixture of chloride of sodium and sulphate of potassium, when both mixtures are in the state of solution. With two acids greatly unequal in their affinity for bases, however, the result might possibly be different.

In some cases, diffusion is also capable of effecting the decomposition of chemical compounds. Thus, when a solution of common alum is allowed to diffuse into water, the sulphate of potassium passes out more rapidly than the sulphate of aluminium. A solution of sulphate of potassium in lime-water left to diffuse into lime-water yields a diffusate containing hydrate of potassium; similarly with sulphate of sodium. The sulphates of potassium and sodium are also decomposed by carbonate of calcium dissolved in carbonic acid water, when the liquid is allowed to diffuse into pure water. The chlorides of potassium and sodium are not sensibly decomposed by lime-water in this manner. When saturated solutions of lime-water and sulphate of calcium are mixed in equal volumes, 1 per cent. of chloride of sodium dissolved in the mixture, and the solution left to diffuse into pure water, scarcely a trace of hydrate of sodium is obtained; but when the solution of sulphate of calcium, with an addition of 2 per cent. of chloride of sodium, is kept at the boiling point for half an hour, and the solution mixed two or three days afterwards with an equal volume of lime-water, and diffused into pure water for 3½ days, the diffusate in three cells is found to contain 0·234 grains hydrate of sodium and 0·371 sulphate of sodium. It appears, then, that more than one condition of equilibrium is possible for mixed solutions of sulphate of calcium and chloride of sodium. Cold solutions of these salts may be mixed without decomposition, or without sensible formation of sulphate; but, on heating, this change is induced, and is permanent, sulphate of sodium being formed, and continuing to exist in the cold solution; for it is the decomposition of that salt alone by hydrate of calcium which appears to yield the diffused hydrate of soda. As the effects of time and temperature are often convertible, it is possible that the same decomposition might take place at ordinary temperatures after a considerable time. If such be the case, we have an agency in the soil by which the alkaline carbonates required by plants may be formed from the chlorides of potassium and sodium, as well as from the sulphates; for the sulphate of calcium, generally present, will convert those chlorides into sulphates. The mode in which the soil of the earth is moistened by rain is peculiarly favourable to separations by diffusion. The soluble salts of the soil may be supposed to be carried down together, to a certain depth, by the first portion of rain which falls, while they find afterwards an atmosphere of nearly pure water, in the moisture which falls last and occupies the surface stratum of the soil. Diffusion of the salts upwards into the water, with its separations and decompositions, must necessarily ensue. The salts of potassium and ammonium, which are most required for vegetation, possess the highest diffusibility, and will rise first. The pre-eminent diffusibility of the alkaline hydrates may also be called into action in the soil by hydrate of calcium, particularly as quicklime is applied as a top-dressing to grass-lands. (Graham.)

4.—Dialysis.

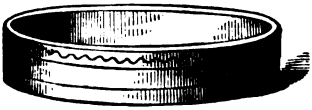
Membranes or septa of the colloïd class (p. 710) possess a property which is very useful in assisting diffusive separations. The jelly of starch, that of animal mucus, of pectin, of Payen's vegetable gelose (ii. 826), and other solid colloïdal hydrates, all of which are strictly speaking insoluble in cold water, are themselves permeable when in mass, as water is, by the more highly diffusive substances. But such jellies greatly resist the passage of the less diffusive substances, and cut off entirely other colloïd substances like themselves that may be in solution: in this respect they resemble animal membrane. This mode of separation by diffusion through a septum is called dialysis. A mere film of the colloïdal septum produces this separating effect. Thus, if a sheet of very thin letter-paper, well sized with starch, and having no porosity, be laid on the surface of water, a depression made in its centre, and a mixed solution of cane-sugar and gum-arabic containing 5 per cent. of each substance poured upon it, the sugar diffuses through into the water while the gum remains above, so that, after twenty-four hours, the water below is found to contain about three-fourths of the whole sugar, in a condition so pure as to crystallise when the liquid is evaporated over the water-bath. Now the sized paper has no power to act as a filter; it is mechanically impenetrable, and refuses a passage to the mixed liquid as a whole. Molecules only permeate this septum, and not masses. The molecules also are moved by the force of diffusion. But the water of the gelatigenous starch with which the paper is sized, is not directly available as a medium for the diffusion of either the sugar or the gum, being in a state of real though feeble chemical combination. The hydrated compound itself is solid, and also insoluble. Sugar, however, with other crystalloïds, can separate water, molecule after molecule, from any hydrated colloïd, such as starch. The sugar thus obtains the liquid medium required for diffusion, and makes its way through the gelatinous septum. Gum, on the other hand, presenting, as a colloïd, an affinity for water of the feeblest description, is unable to separate that liquid from the gelatinous starch, and so fails to open the door for its own passage outwards by diffusion.

Diffusion of a crystalloïd through a firm jelly appears to proceed at nearly the same rate as into pure water. This is strikingly shown by the following experiment.

Ten grammes of chloride of sodium and 2 grammes of the Japanese gelatin, or gelose of Payen, were dissolved together in so much hot water as to form 100 cub. cents. of liquid. Introduced into the empty diffusion-jar and allowed to cool, this liquid set into a firm jelly, occupying the lower part of the jar, and containing of course 10 per cent. of chloride of sodium. Instead of placing pure water over this jelly, it was covered by 700 cub. cents. of water containing 2 per cent. of the same gelose, cooled so far as to be on the point of gelatinising, the jar at the same time being placed in a cooling mixture in order to expedite that change. The jar with its contents was now left undisturbed for eight days at the temperature 10°. After the lapse of this time, the jelly was removed from the jar in successive portions of 50 cub. cents. each from the top, and the proportion of chloride of sodium in the various strata ascertained. The results were very similar to those obtained in diffusing the same salt in a jar of pure water, excepting that the diffusion in the gelose appeared more advanced in eight days than diffusion in water for seven days. With a coloured crystalloïd, such as acid chromate of potassium, the gradual elevation of the salt to the top of the jar is very plainly seen. On the other hand, the diffusion of a coloured colloïd, such as caramel, through the jelly, appears scarcely to have begun after the lapse of eight days. The diffusion of a salt into the solid jelly may be regarded as cementation in its simplest form.

The most suitable of all substances for a dialytic septum is De la Rue's vegetable parchment or parchment-paper (i. 819), which is unsized paper, altered by a short immersion in sulphuric acid, or in chloride of zinc. Paper so metamorphosed acquires considerable tenacity, and when wetted, expands and becomes translucent, evidently admitting of hydration. In the wetted state, parchment-paper can easily be applied to a light hoop of wood, or better, to a hoop made of sheet gutta percha, 2 inches in depth and 8 or 10 inches in diameter, so as to form a vessel like a sieve in form (*fig.* 710). The disc of parchment-paper used should exceed in diameter the hoop to be covered by 4 inches, so as to rise well round the hoop. It may be bound to the hoop by string, or by an elastic band, but should not be firmly secured. The parchment-paper must not be porous. Its soundness will be ascertained by sponging the upper surface with pure water, and then observing that no wet spots show themselves on the opposite side. Such defects may be remedied by applying liquid albumin, and then coagulating the same by heat. Mr. De la Rue recommends the use of albumin in cementing parchment-paper, which may thus be formed into cells and bags very useful in dialytic experiments. The mixed fluid to be dialysed is poured into the hoop upon the surface of the parchment-paper to a small depth only, such as half an inch. The vessel described (*dialyser*) is then floated in a basin containing a considerable volume of water, in order to induce the egress of the diffusive constituents of the mixture. Half a litre of urine, dialysed for twenty-four hours, gave its crystalloïdal constituents to the external water. The latter, evaporated by a water-bath, yielded a white saline mass. From this mass urea was extracted by alcohol in so pure a condition as to appear in crystalline tufts upon the evaporation of the alcohol.

Fig. 710.



For operating on smaller quantities of liquid, a small glass bell jar, tied round at the bottom, as shown in *fig.* 711, may be used. *Figs.* 712, 713 show convenient modes of supporting the instrument in a basin or a jar of water. In Mr. Graham's experiments two sizes of bulb were employed, 3·14 and 4·44 inches in diameter, the dialytic septa having areas very nearly of $\frac{1}{100}$ and $\frac{1}{200}$ of a square metre (15·6 and 7·8 square inches). With 100 cub. cents. of liquid (the quantity usually employed) the septum of the smaller instruments was covered to the depth of 20 mm. (0·8 inch) and the septum of the larger to a depth of 10 mm. (0·4 inch). The thinner the stratum, the more exhaustive the diffusion in a given time. When a considerable diffusion is desired within 24 hours, it is generally inadvisable to cover the septum deeper than 10 or 12 mm. (half an inch).

Fig. 711.

Fig. 712.

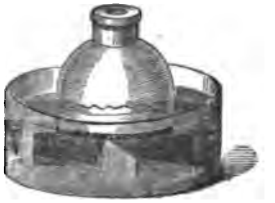
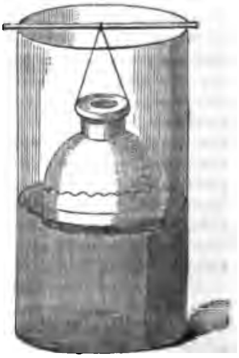


Fig. 713.



Numerous experiments on the diffusion of crystalloïds through various dialytic septa, such as gelatinous starch, coagulated albumin, gum-tragacanth, besides animal mucus and parchment-paper, all tended to prove how little the diffusive process is interfered with by the intervention of colloïd matter. Salts appear to preserve their usual relative diffusibility unchanged. The same partial separation of mixed salts is observed as in the water-jar (p. 713). With a mixture, for instance, of equal parts of chlorides of potassium and sodium in a dialyser, the first tenth part of the mixture which passed through was found to consist of 59·17 per cent. of chloride of potassium and 40·83 per cent. of chloride of sodium. Double salts also, such as alum, and the sulphate of copper and potassium, which admit of being resolved into pairs of unequally diffusive salts, were largely decomposed upon the dialyser, as they are in the water-jar. The effect of heat in promoting diffusion appears, however, to be diminished in dialysis, at least with a parchment-paper septum. Thus the diffusion from a 2 per cent. solution of chloride of sodium, in a constant period of three hours, was—

		Ratio.
At 10° C. . . .	0·738 grm.	1·00
„ 20 . . .	0·794 grm.	1·07
„ 30 . . .	0·892 grm.	1·20
„ 40 . . .	1·017 grm.	1·37

The rate of diffusion in water alone, without the septum, would have been doubled by an equal rise of temperature, instead of being increased one-third only as above.

The following table exhibits the rate of diffusion of several substances, both crystalloïds and colloïds, compared with chloride of sodium as a standard. The larger bell-jar (p. 716) was used, and the parchment-paper was changed in each experiment. The substance in solution amounted to 2 grms., the depth of liquid in the dialyser to 10 mm. (0·4 of an inch), and the surface of the septum to 0·01 square metre (15·6 square inches).

TABLE VII.—*Dialysis through Parchment-paper during twenty-four hours, at* 12°.

Two per cent. solutions.	Diffusate in grammes.	Proportional diffusate.
Chloride of sodium . . .	1·657	1·000
Picric acid	1·690	1·020
Ammonia	1·404	·847
Theine	1·166	·703
Salicin	·835	·503
Cane-sugar	·783	·472
Amygdalin	·517	·311
Extract of quercitron . .	·305	·184
Extract of logwood . . .	·280	·168
Catechu	·265	·159
Extract of cochineal . . .	·086	·051
Gallotannic acid . . .	·050	·030
Extract of litmus . . .	·033	·019
Purified caramel . . .	·009	·005

The picric acid and theine were actually diffused from 1 per cent. solutions, and the numbers observed are multiplied by 2. The crystallisable principles, theine, salicin, and amygdalin, appear greatly more diffusible than gallo-tannic acid, or than gum, as has been already seen. Such inequality of rate is likely to facilitate the separation of vegetable principles by the agency of dialysis.

Preparation of Colloïd Substances by Dialysis.

The purification of many colloïd substances may be effected with great advantage by placing them on the dialyser. Accompanying crystalloïds are eliminated, and the colloïd is left behind in a state of purity. The purification of soluble colloïds can rarely be effected by any other known means, and dialysis is evidently the appropriate mode of preparing such bodies free from crystalloïds.

When the mixed solution obtained by pouring silicate of sodium into water acidulated with hydrochloric acid, was placed upon a parchment-paper dialyser, and allowed to diffuse into water, the latter being occasionally changed, a quantity of silicic acid was left upon the septum, amounting, after the lapse of five days, to seven-eighths of the original silicic acid, and the solution of silicic acid which subsequently passes through, is so free from hydrochloric acid and chloride of sodium as not to give a precipitate with nitrate of silver.

Soluble silicic acid forms a peculiar class of compounds, which like itself, are colloïdal, and differ entirely from the ordinary silicates. These compounds, which may be called **collisilicates** or **co-silicates**, appear to contain an acid of higher atomic weight than ordinary silicic acid. Cosilicic acid, like gallotannic, gummic, and other colloïdal acids, unites with *gelatin*, forming a cosilicate of gelatin, which is precipitated on mixing the solutions of silicic acid and gelatin; but, like the gallotannate (i. 828), varies in composition according as the one or the other constituent is present in excess. Cosilicic acid also precipitates both *albuminic acid* and pure *casein*.

The true **hydrated alumina**, also Crum's **metalumina** (i. 159), are obtained soluble by dialysing solutions of these oxides in the chloride and acetate of the same metal; so, likewise, **hydrated ferric oxide**, and the peculiar ferric hydrate (metaferric hydrate) discovered by Péan de St.-Gilles (p. 395), and soluble **chromic hydrate** (ii. 949). The several varieties of Prussian blue (ii. 229, 244) are obtained soluble by dialysing their solutions in oxalate of ammonium, the latter salt diffusing away. **Stannic** and **metastannic acids** both give soluble modifications when dialysed from alkaline solutions; **titanic acid**, when dialysed from a solution in dilute hydrochloric acid; **tungstic acid** and **molybdic acids**, when the tungstate and molybdate of sodium in dilute solution are repeatedly dialysed with a slight excess of hydrochloric acid. (Chem. Soc. J. [2] ii. 318.)

A solution of **gum-arabic** (gummate of calcium) dialysed after addition of hydrochloric acid, gave at once the pure gummic acid of Frémy (ii. 955). Soluble **albumin** is obtained in a state of purity by dialysing albumin with addition of acetic acid.

Caramel of sugar purified by repeated precipitation with alcohol, and afterwards by dialysis, contains the proportion of carbon in the highest of the caramelic bodies of Gélis (ii. 748); it forms a tremulous jelly when concentrated, and appears decidedly colloïdal. Like all other colloïds, it has a soluble and an insoluble modification. The latter has its solubility restored by the action of alkalis, followed by that of acetic acid and subsequent dialysis.

For further details on the preparation of colloïds by dialysis, see Chem. Soc. J. xv. 243—260; also the descriptions of the several substances in their alphabetical order in this Dictionary.

Separation of Arsenious Acid from Colloïdal Liquids.—Dialysis may be advantageously applied to the separation of **arsenious acid** and **metallic salts** from organic solutions in medico-legal enquiries. The process has the advantage of introducing no metallic substance or chemical reagent of any kind into the organic fluid. The arrangement for operating is also of the simplest nature.

The organic liquid is placed, to the depth of half an inch, on a dialyser formed of a hoop of gutta percha 10 or 12 inches in diameter, covered with parchment-paper (*fig.* 710, p. 716). The dialyser is then floated in a basin containing a volume of water about four times greater than the volume of organic fluid in the dialyser. The water of the basin is generally found to remain colourless after the lapse of 24 hours; and after being concentrated by evaporation, it admits of the application of the proper reagents to precipitate and remove a metal from solution. One-half to three-fourths of the crystalloïdal and diffusible constituents of the organic liquid will generally be found in the water of the basin.

Tartar-emetic and **strychnine** may be separated from viscid organic matter in a similar manner: indeed, all soluble poisonous substances appear to be crystalloïds, and therefore pass through colloïdal septa.

LIQUIDS, DISPERSIVE POWERS OF. See LIGHT (p. 624).

LIQUIDS, EXPANSION OF. See HEAT (p. 52).

LIQUIDS, INDICES OF REFRACTION OF. See LIGHT (pp. 615, 627).

LIQUIDS, OSMOSE OF. When two liquids are separated by the intervention of a porous diaphragm, a flow of liquid takes place from one side of the septum to the other, or sometimes an unequal flow of the two liquids in opposite directions, so that the quantity of liquid increases on one side of the septum and diminishes on the other. This phenomenon was originally designated by the correlative terms **Endosmose** and **Exosmose**, but it is better expressed by the shorter word (**Osmose**, from ὠσμός, impulsion), which includes the two former.

The passage of liquids through porous septa was first studied by **Dutrochet**, whose apparatus, called an *endosmometer*, consisted of a narrow glass tube, having a funnel-shaped expansion at the bottom, and closed at that end by a piece of bladder. This tube was filled with a saline solution, and placed in a vertical position in a jar containing water. The flow of liquid in the one direction or the other was measured by the rise or fall of the liquid in the tube. Dutrochet inferred, from his experiments, that the velocity of the osmotic current is proportionate to the quantity of salt or other solid substance originally contained in the saline solution. The experiments were, however, inexact, because no allowance was made for the alteration of hydrostatic pressure caused by the rise or fall of the liquid in the tube. **Vierordt** (Pogg. Ann. lxxxiii. 79), who used a modification of Dutrochet's apparatus, in which this source of error was removed, found that the velocity of the current increases with the initial concentration of the solution, but in a lower ratio.

Professor Jolly, of Heidelberg, has examined the osmose of water and saline solutions by a different method. The saline solution containing a known quantity of salt is contained in a glass tube closed at the bottom with bladder, and plunged into water, which is frequently changed, so as to keep it nearly pure. The tube with its contents is taken out from time to time and weighed, and these operations are repeated till the weight becomes constant, showing that the whole of the salt has passed out from the tube, and nothing but water remains.

In this manner it is found that a given quantity of any salt which passes through the septum into the water is always replaced by a definite quantity of water. The quantity of water which is thus replaced by a unit of weight of the salt, is called the *endosmotic* (or *osmotic*) *equivalent* of that salt. This quantity varies with the nature of the salt, and with the temperature, increasing as the temperature rises; but it is independent of the density of the solution. At temperatures near 0° C., the endosmotic equivalent of hydrate of potassium was found to be 200; of chloride of sodium, between 4·3 and 4·6; of sulphate of sodium, between 11 and 12; of neutral sulphate of potassium, 12; of acid sulphate of potassium, 2·3; and of hydrated sulphuric acid (at 18° C.), 0·35.

These results point to the conclusion, that the osmose between water and saline solutions consists, not in the opposite passage of two liquid currents, but in the passage of particles of the salt in one direction, and of pure water in the other. This conclusion is strengthened by Graham's observation, that common salt diffuses into water, through a thin membrane of ox-bladder deprived of its outer muscular coating, at the same rate as when no membrane is interposed.

The flow of water into the saline solution is the only one of the two movements which can be correctly described as a current. This is, in fact, the true osmose, and depends essentially on the action of the membrane or other porous septum; for the quantity of water which thus passes into the solution is often much greater than would be introduced by mere liquid diffusion, amounting in some cases to several hundred times that of the salt displaced.

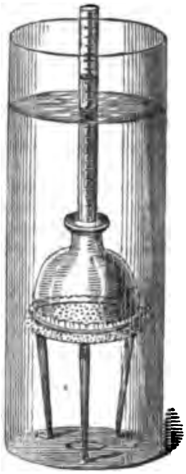
This action of the septum has been explained in various ways. By Dutrochet and others, it was attributed to capillarity; but this force is quite insufficient to account for the great inequality of ascension which different liquids exhibit in the osmotic apparatus: in fact, Graham has shown, that solutions of the most different character exhibit very nearly equal ascension in tubes of equal diameter.

Osmose has likewise been attributed to the unequal absorption of the two liquids by the porous septum. Suppose the septum to be of such a nature as to absorb only one of the liquids,—the water, for instance. The water will then penetrate the septum, and coming in contact with the saline solution, will diffuse into it. More water will then be absorbed, and subsequently diffused, and thus a continuous current will be set up. If both liquids are absorbed by the septum, but in different degrees, and each is capable of diffusing into the other, like water and alcohol, the result will be the formation of two unequal currents in opposite directions. Water is absorbed by animal membrane much more rapidly than most other liquids, and accordingly, when a septum of this kind is used, the direction of the current is in most cases from the water to the other liquid. According to Liebig, a given weight of dried ox-bladder absorbs in the same time, 200 vols. of water, 133 vols. of a saturated solution of common salt, 38 vols. of alcohol of the strength of 84 per cent., and 17 vols. of bone-oil. When water and alcohol are separated by an animal membrane, the quantity of water which passes into the alcohol is greater than the quantity of alcohol which passes into the water; but when the same liquids are divided by a thin film of collodion, which absorbs alcohol more quickly than water, the contrary effect is produced.

On the other hand, the numerous experiments recently made by Graham (Phil. Trans. 1855, p. 177; Chem. Soc. J. viii. 43) lead to the conclusion that osmose depends essentially on the chemical action of the liquid on the septum. These experiments were made partly with porous mineral septa, partly with animal membrane. The earthenware osmometer consisted of the porous cylinders employed in voltaic batteries, about five inches in depth, surmounted by a glass tube 0· inch in diameter, attached to the mouth of the cylinder by means of a cap of gutta percha. The cylinder was filled to the base of the glass tube with a saline solution, and immediately placed in a jar of distilled water; and as the liquid within the instrument rose during the experiment, water was added to the jar to equalise the pressure. The rise (or fall) of the liquid in the tube was very regular, as observed from hour to hour, and the experiment was generally terminated in five hours. From experiments made on solutions of every variety of soluble substance, it appeared that the rise or osmose is quite insignificant with neutral organic substances in general, such as sugar, alcohol, urea, tannin, &c.; so likewise with neutral salts of the earths and ordinary metals, with the chlorides and nitrates of potassium and sodium, and with chloride of mercury. A more sensible but still very moderate osmose is exhibited by hydrochloric, nitric, acetic, sulphurous, citric, and tartaric acids. These are surpassed by the stronger mineral acids, such as sulphuric acid, phosphoric, and by sulphate of potassium, which are again exceeded by salts of potassium and sodium, possessing a decided acid or alkaline reaction, such as dioxalate of potassium, phosphate of sodium, or the carbonates of potassium and sodium. The highly osmotic substances were also found to act with most advantage in small proportions—producing, in fact, the largest osmose in the proportion of one-quarter per cent. dissolved. The same substances are likewise always chemically active bodies, and possess affinities which enable them to act on the material of the earthenware septum. Lime and alumina were always found in solution after osmose, and the corrosion of the septum appeared to be a necessary condition of the flow. Septa of other materials, such as pure carbonate of calcium, gypsum. compressed charcoal, and tanned sole-leather, although not deficient in porosity, gave no osmose apparently, because they are not chemically acted on by the saline solutions.

Similar results were obtained with septa of animal membrane. Ox-bladder was found to act with much greater strength and regularity when divested of its outer muscular coat. Cotton calico, impregnated with liquid albumin, and afterwards heated to coagulate the albumin, formed an excellent septum, resembling membrane in every respect. The osmometer (*fig.* 714) used in these experiments was arranged like the original instrument of Dutrochet; but the membrane was supported by a plate of perforated zinc, and the tube was of considerable diameter, viz. one-tenth of that of the mouth of the bulb, or of the disc of membrane exposed to the liquids.

Fig. 714.



Osmose in membrane presents many points of similarity to that in earthenware. The membrane is constantly undergoing decomposition, and its osmotic action is exhaustible. Salts and other substances capable of determining a large osmose are all chemically active substances, while the great mass of neutral organic substances and perfectly neutral monobasic salts of the metals, such as chloride of sodium, possess only a low degree of action, or are wholly inert. The active substances are also most efficient in small proportions.* With a solution containing $\frac{1}{10}$ per cent. of carbonate of potash, the rise in the osmometer was 167 millimetres; and with 1 per cent. of the same salts, 206 millimetres in five hours. With another membrane and a stronger solution, the rise was 863 millimetres, or upwards of 38 inches in the same time. To induce osmose, the chemical action on the membrane must be different on the two sides, and apparently not in degree only, but in kind, viz. an alkaline action on the albuminous substance of the membrane on the one side and an acid action on the other. The water appears always to accumulate on the alkaline or basic side of the membrane. Hence with an alkaline salt, such as carbonate of sodium, in the osmometer, and water outside, the flow is inwards; but with an acid in the osmometer, there is negative osmose, or the flow is outwards, the liquid then falling in the tube. The chlorides of barium, sodium, and magnesium, and similar neutral salts, are wholly indifferent, or appear to act merely in a subordinate manner to some other active acid or basic substance, which may be present in the solution or the membrane in the most minute quantity. Salts which admit of division into a basic salt and free acid exhibit an osmotic activity of the highest order, *e.g.* the acetate and various other salts of alumina, ferric oxide and chromic oxide, cuprous chloride, stannous chloride, nitrate of lead, &c. The acid travels outwards by diffusion, superinducing a basic condition of the inner surface of the membrane, and an acid condition of the outer surface, the most favourable condition for a high positive osmose. Again, the dibasic salts of potassium and sodium, such as the sulphate and tartrate, though strictly neutral in properties, begin to exhibit a positive osmose, in consequence, perhaps, of their resolution into an acid supersalt and free alkaline base.

The following table exhibits the osmose of substances of all classes through membrane, the degree being a rise or fall of 1 millimetre:—

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* The action increases with the strength of the solution up to a certain point, as the above examples show. With stronger solutions the pores of the membrane probably becomes topped up with particles of salt, and the action consequently diminishes.

Osmose of 1 per cent. Solutions in Membrane.

	Degrees.		Degrees.
Oxalic acid	− 148	Chloride of zinc	+ 54
Hydrochloric acid (0·1 per cent.)	− 92	Chloride of nickel	88
Trichloride of gold	− 54	Nitrate of lead	125 to 211
Stannic chloride	− 46	Nitrate of cadmium	137
Platinic chloride	− 30	Nitrate of uranium	234 to 458
Chloride of magnesium	− 3	Nitrate of copper	204
Chloride of sodium	+ 2	Chloride of copper	351
Chloride of potassium	18	Stannous chloride	289
Nitrate of sodium	2	Ferrous chloride	435
Nitrate of silver	34	Mercuric chloride	121
Sulphate of potassium	21 to 60	Mercurous nitrate	356
Sulphate of magnesium	14	Mercuric nitrate	476
Chloride of calcium	20	Ferric acetate	194
Chloride of barium	21	Acetate of aluminium	280 to 393
Chloride of strontium	26	Chloride of aluminium	540
Chloride of cobalt	26	Phosphate of sodium	311
Chloride of manganese	34	Carbonate of potassium	439

The osmotic action of carbonate of potassium and other alkaline salts is interfered with in an extraordinary manner by the presence of chloride of sodium, being reduced to almost nothing by an equal proportion of that salt. The moderate positive osmose of sulphate of potassium is converted into a very sensible negative osmose by the presence of the merest trace of a strong acid, while the positive osmose of the same salt is singularly promoted by a small proportion of alkaline carbonate: thus, a 1 per cent. solution of sulphate of potassium gives an osmose of 21°, but the addition of 0·1 per cent. of carbonate of potassium raises it to between 254 and 204 degrees. (Graham.)

If a glass tube, bent in the form of a siphon, and having its shorter leg closed with bladder, be partially filled with salt water, the shorter leg then immersed in a vessel of pure water, and mercury poured into the longer leg, so that its pressure may act in opposition to the force with which the water tends to enter the saline solution through the bladder, it will be found that, when the column of mercury attains a certain height, the two liquids will mix without change of volume, the force of the osmotic current being then exactly balanced by the weight of the mercurial column. In this way the mechanical force of the osmotic current may be measured. (Liebig.)

Osmose appears to play an important part in the functions of life. We have seen that it is peculiarly excited by dilute saline solutions, such as the animal and vegetable juices are, and that the acid or alkaline property which these juices possess is another favourable condition for their action on membrane. The natural excitation of osmose in the substance of the membranes or cell-walls dividing such solutions seems therefore almost inevitable.

In osmose there is also a remarkably direct substitution of one of the great forces of nature by its equivalent in another force,—the conversion, namely, of chemical action into mechanical power. Viewed in this light, the osmotic injection of fluids may, perhaps, supply the deficient link which intervenes between chemical decomposition and muscular movement. The ascent of the sap in plants appears to depend upon a similar conversion of chemical, or, at least, molecular action into mechanical force. The juices of plants are constantly permeating the coatings of the superficial vessels in the leaves and other organs; and as these evaporate into the air, a fresh portion of liquid is absorbed by the membrane and evaporates; and thus a regular upward current is established, by which the sap is transferred from the roots to the highest parts of the tree. In a similar manner, the evaporation constantly taking place from the skin and lungs of animals, causes a continuous flow of the animal juices from the interior towards the surface.

From his recent experiments on the passage of liquids through colloïdal septa, Graham infers that the water movement in osmose is an affair of hydration and of dehydration in the substance of the membrane or other colloïd septum, and that the diffusion of the saline solution placed within the osmometer has little or nothing to do with the osmotic result, otherwise than as it affects the state of hydration of the septum.

Osmose is generally considerable through membraneous and other highly hydrated septa, with the solution of any colloïd (gum, for instance) contained in the osmometer. Yet the diffusion outwards of the colloïd is always minute, and may sometimes amount to nothing. Indeed, an insoluble colloïd, such as gum-tragacanth, placed in powder within the osmometer, was found to indicate the rapid entrance of water, to convert the gum into a bulky gelatinous hydrate. Here no outward or double movement is possible.

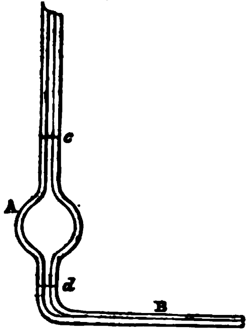
The degree of hydration of any gelatinous body is much affected by the liquid medium in which it is placed. This is very obvious in fibrin and animal membrane. Placed in pure water, such colloïds are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water, tends to hydrate itself in a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane and reaches the inner surface, it there receives a check. The degree of hydration is lowered, and water must be given up by the inner layer of the membrane, and it forms the osmose. The contact of the saline fluid is thus attended by a continuous catalysis of the gelatinous hydrate, by which it is resolved into a lower gelatinous hydrate and free water. The inner surface of the membrane of the osmometer contracts by contact with the saline solution, while the outer surface dilates by contact with pure water. Far from promoting this separation of water, the diffusion of the salt throughout the substance of the membrane appears to impede osmose, by equalising the condition as to saline matter of the membrane through its whole thickness. The advantage which colloïdal solutions have in inducing osmose, appears to depend in part upon the low diffusibility of such solutions, and their want of power to penetrate the colloïdal septum.

The substances fibrin, albumin, and animal membrane swell greatly when immersed in water containing minute proportions of acid or of alkali, as is well known. On the other hand, when the proportion of acid or alkali is carried beyond a point peculiar to each substance, contraction of the colloïd takes place. Such colloïds as have been named, acquire the power of combining with an increased proportion of water, and of forming superior gelatinous hydrates, in consequence of contact with dilute acid or alkaline reagents. Even parchment-paper is more elongated in an alkaline solution than in pure water. When so hydrated and dilated, the colloïds present an extreme osmotic sensibility. Used as septa, they appear to assume or resign their water of gelatination under influences apparently the most feeble. It is not attempted to explain this varying hydration of colloïds with the osmotic effects thence arising. Such phenomena belong to colloïdal chemistry, where the prevailing changes in composition appear to be of the kind vaguely described as catalytic. To the future investigation of catalytic affinity, therefore, must we look for the further elucidation of osmose. (Graham, Chem. Soc. J. xv. 268.)

LIQUIDS, TRANSPIRATION OF. (Poiseuille, Ann. Ch. Phys. [3] vii. 50; xxi. 76; Jahresber. 1847–8, p. 139; Graham, Phil. Trans. 1861, p. 373; Chem. Soc. J. xv. 427.)—This term is applied to the passage of liquids through capillary tubes under pressure, in accordance with the analogy of gaseous transpiration (ii. 820). The first experiments on the subject were made by Poiseuille, who determined the manner in which the flow of the liquid is related to the pressure, and to the length and diameter of the tubes; also, in many cases, the manner in which it is affected by the nature of the liquid. Graham's enquiries were directed chiefly to the relation between the rate of transpiration and the chemical composition of the liquid.

The apparatus used by both these enquirers consists essentially of a small but rather stout glass bulb, A (*fig.* 715), about two-thirds of an inch in diameter, having a capacity of from 4 to 8 c. c., blown upon a thick glass tube, with a bore of about 2 millimetres. A scratch *c* is made upon the glass tube above, and another *d* below the bulb, to indicate the available capacity of the instrument. The lower tube is bent at a right angle to the upper, and a fine capillary tube, B, from 3 to 4 inches in length, is sealed to the curved extremity of the tube. The bulb and capillary are immersed in a vessel of water during the experiment, to secure uniformity of temperature. The force employed to impel the liquid through the capillary is obtained from compressed air contained in a large reservoir provided with a mercurial gauge. The time is noted in seconds.

Fig. 715.



The liquid may be introduced into the bulb through the open upper tube by means of a tube-funnel; but it is more convenient, although requiring a much longer time, to fill the bulb by aspiration through the capillary. With this view, the compressed air is shut off by a stop-cock, and the upper tube of the bulb allowed to communicate with the receiver of an air-pump instead, whereby exhaustion is produced, while the open end of the capillary is immersed in a portion of the liquid. The liquid which enters the bulb in this manner is sure to be free from any solid matter that could cause obstruction in the capillary during the subsequent passage of the liquid outwards, while the disconnecting of the bulb from the rest of the apparatus, for the purpose of filling the former, is also avoided.

From the experiments of Poiseuille it appears that when a tube exceeds a certain length (which is greater as the diameter increases), the rate of efflux is regulated by the following laws:—

1. The flow increases directly as the pressure.
2. With tubes of equal diameter, the quantities discharged in equal times are inversely as the lengths.
3. In tubes of equal length, but different diameters, the rate of efflux is as the fourth powers of the diameters.

The material of which the tube is made does not appear to influence the result, but the nature of the liquid employed exercises a marked effect. The liquids used in Poiseuille's experiments were in most cases aqueous solutions of various bodies, especially of salts. In the majority of instances, the flow of the solution was slower than that of distilled water. All the alkalis occasioned this retardation. In a few instances, no sensible alteration was produced; thus neither nitrate of silver, mercuric chloride, iodide of sodium, iodide of iron, nitric, hydriodic, bromic, nor hydrobromic acid seemed to have any influence, whilst sulphydric and prussic acids, the nitrates and chlorides of potassium and ammonium, and the iodide, bromide, and cyanide of potassium, increased the rapidity of the flow; it is remarkable, however, that concentrated solutions of iodide of potassium, at temperatures above 60°, and of nitrate of potassium above 40°, actually flow more slowly than distilled water. Strict attention to the temperature at which these comparisons are made is absolutely necessary; for both with water and with dilute solutions generally, a slight elevation of temperature produces a great increase in the rapidity of efflux. Water, for instance, at 45° escapes through the same tube 2½ times as fast as it does at 5°.

No connection has hitherto been traced between the rate of efflux of a liquid and its density, capillarity, or fluidity. The capillarity of alcohol, as well as its density, increases in proportion as it is diluted with water, whilst its fluidity diminishes; but a mixture of equal parts of alcohol and water flows out with considerably less than half the rapidity of pure alcohol, and with less than a third of that of distilled water. The dilution of alcohol therefore, to a great extent, retards its efflux, and beyond that point increases it: the minimum rate of efflux corresponds with that particular mixture of alcohol and water, which is attended with the maximum contraction after the admixture of the two liquids.

The degree of solubility of a body in water appears to exercise but a secondary influence on the result. Poiseuille shows it to be highly probable that various solutions, when introduced into the blood of a living animal, provided they do not cause the serum to coagulate, produce effects of acceleration and retardation on the capillary circulation corresponding with those which are observed in the same liquids in capillary tubes of glass. He has shown this to be the case, by direct experiment, with iodide of potassium when injected into the veins of the horse; and that when various salts are mingled with the serum, and the liquids are allowed to flow out through small tubes, retardation or acceleration occurs, as in the corresponding cases, with their aqueous solutions.

The following tables contain the numerical results of Poiseuille's experiments.

The salts are arranged according to the acids, which appear to have the greatest influence on the rate of efflux. The letters *A*, *B*, *C*, &c., designate the tubes employed. L is the length, D the diameter of the tube, H the pressure, measured by a column of water in millimetres, T the temperature (centigrade), M the quantity of substance in 100 pts. of water, S the time of efflux in seconds. The figures printed in the thicker type denote the time of efflux of pure water in each case.

Flow of Liquids through Capillary Tubes. (Poiseuille.)

Substance.	M.	S.	Substance.	M.	S.
B. L = 64; D = 0·24946; H = 1000; T = 11·6°.			*B.* L = 64; D = 0·24946; H = 1000; T = 11·6°.		
Iodide of potassium	0	**568·3**	Iodide of potassium	10·0	530·4
" "	0·1	567·6	" "	20·0	505·7
" "	0·2	566·7	" "	50·0	474·9
" "	0·4	565·6	Iodide of sodium	0	**569·5**
" "	0·8	563·5	" "	0·4	569·6
" "	2·0	557·6	" "	2·0	569·8

Flow of Liquids through Capillary Tubes—continued.

Substance.	M.	S.
B. L = 64; D = 0·24946; H = 1000; T = 11·6°.		
Iodide of sodium .	10·0	570·0
" " . .	20·0	577·1
Iodine . . .	0	568·3
" . . .	sat.	568·7
Iodide of iron . .	0·2	568·2
" " . .	10·0	568·5
Bromide of potassium	0·4	565·8
" " .	2·0	560·0
" " .	10·0	537·6
T = 11·2°.		
Nitrate of potassium .	0	575·8
" " .	0·1	574·5
" " .	0·2	573·5
" " .	0·4	571·4
" " .	1·0	564·5
" " .	10·0	541·2
" " .	20·0	533·3
" of ammonium	1·0	569·4
" " .	10·0	531·1
" of sodium .	1·0	575·9
" " .	10·0	592·4
" of lead . .	1·0	577·8
" " . .	4·0	582·9
" of strontium .	1·0	578·8
" " .	4·0	586·7
" of calcium .	1·0	581·2
" " .	10·0	623·6
" of magnesium	1·0	583·2
" " .	10·0	641·7
C. L = 37; D = 0·19495; H = 1370·8; T = 14·2°.		
Nitrate of silver . .	0	741·5
" " . .	1·0	740·9
" " . .	10·0	741·0
B. H = 1000; T = 11·9°.		
		565·0
Chloride of potassium	1·0	560·8
" " .	10·0	544·8
" of ammonium	1·0	560·9
" " .	2·0	556·5
" " .	10·0	535·8
" of sodium .	1·0	569·4
" " .	10·0	640·3
" of calcium .	1·0	571·2
" " .	10·0	620·7
" of magnesium	1·0	574·9
" " .	10·0	646·8
B. H = 865·1; T = 11·2°.		
Mercuric chloride .	0	608·5°
" " .	10	608·1
" " .	20	607·9
" " .	sat.	607·8
B. H = 1000; T = 11·2°.		
		575·8
Hydrochlorate of morphine . . .	1·25	589·8
Hydrochlorate of strychnine . .	1·4	590·0
T = 12·7°.		
		554·0
Cyanide of potassium	1·0	551·6
" " .	4·0	548·8
" of mercury .	1·0	558·4
" " .	4·0	564·3
	to serum:	
Serum . . .		1014·5
Cyanide of potassium	1·0	998·7
" of mercury .	1·0	1025·3
T = 11·2°.		
		575·8
Sulphate of potassium	1·0	578·9
" " .	4·0	592·1
" of ammonium	1·0	582·0
" " .	4·0	598·9
" of sodium .	1·0	590·3
" " .	4·0	606·1
" of magnesium	1·0	590·5
" " .	4·0	630·1
" of zinc . .	2·0	595·6
" of ferrosum .	2·0	609·5
" of morphine .	1·25	590·3
T = 12·7°.		
		575·8
Alum	1·0	592·4
"	4·0	632·4
Phosphate of potassium	1·0	583·4
" " .	4·0	602·7
" of sodium .	1·0	588·6
" " .	4·0	622·8
" of ammonium	1·0	590·2
" " .	4·0	626·2
T = 11·2°.		
		575·6
Arsenate of potassium	1·0	583·3
" " .	2·0	590·8
" of sodium .	1·0	588·0
" " .	4·0	617·3
Acid carbonate of ammonium . . .	1·0	580·6
Acid carbonate of potassium . . .	1·0	580·4
Acid carbonate of sodium . . .	1·0	589·8
Carbonate of ammonium . . .	1·0	583·8
" " "	4·0	602·9
Carbonate of potassium	1·0	588·3
" " .	4·0	617·0
" of sodium .	1·0	592·5
" " .	4·0	622·7

Flow of Liquids through Capillary Tubes—continued.

Substance	M.	S.
T = 11·8°.		
		566·2
Oxalate of potassium .	1·0	571·1
„ „ .	10·0	620·1
„ of ammonium	1·0	574·2
„ „ .	4·0	596·6
„ of sodium .	1·0	578·4
Acid oxalate of potassium . . .	1·0	573·4
B. H = 858; T = 141°.		
		620·0
Acetate of lead . .	1·0	633·1·
„ „ . .	4·0	653·5
B. H = 1000; T = 11·4°.		
		571·0
Citrate of iron . .	2·0	595·3
T = 11·2°.		
		575·8
Tartar-emetic . .	1·0	581·2
„ „ . .	4·0	594·7
D. L = 105; D = 0·17; H = 1998·6; T = 12·8°.		
		123′ 38″
Acetate of ammonium	2·0	122 35
B. H = 1000; T = 11·9°.		
		564·7
Hydrate of potassium .	2·0	579·4
„ of sodium .	2·0	611·4
Concentrated ammonia	10·0	628·7
„ „	pure	725·4
T = 11·2°.		
		574·9
Hydriodic acid . .	1·0	575·0
„ „ . .	4·0	574·5
Nitric „ . .	1·0	573·9
„ „ . .	3·2	574·6
„ „ . .	8·2	573·3
T = 11·8°.		
		566·2
Solid iodic acid . .	1·0	570·1
„ „ . .	3·4	573·5

Substance.	M.	S.
E. L = 27; D = 0·1316; H = 2012·2; T = 10°.		
		499·0
Prussic acid . .	33·3	489·0
F. L = 70; D = 0·207; H = 2 039·4; T = 10°.		
Pure serum		1448
100 water to 100 serum . .		1277
100 prussic acid „ . .		1278
100 sulphydric acid „ . .		1266
B. H = 1000; T = 11·6°.		
		568·3
Hydrobromic acid .	1·0	569·7
„ „ .	7·2	571·4
Bromic acid . .	1·0	569·3
„ „ . .	3·2	570·5
T = 11·2°.		
		575·8
Hydrochloric acid .	1·0	577·3
„ „ .	2·0	579·5
„ „ .	10·0	591·8
„ „ .	20·0	604·3
Carbonic acid . .	sat.	580·5
Artificial Seltzer water	sat.	584·2
Solid oxalic acid . .	1·0	582·9
„ „ . .	2·0	590·6
„ „ . .	10·0	625·7
„ phosphoric acid .	1·0	582·8
„ „ „ .	4·0	603·9
Acetic acid . . .	1·0	585·5
„ . . .	10·0	633·4
„ . . .	pure	1315·0
Solid citric acid . .	1·0	586·0
„ „ „ . .	10·0	682·1
„ arsenic acid .	1·0	586·3
„ „ . .	4·0	618·0
Arsenious acid . .	1·0	578·6
Concentrated sulphuric acid . . .	1·0	589·6
Concent. sulphuric acid	pure	1459·5
Solid tartaric acid .	2·0	601·1
Serum of ox-blood .	pure	1048·5
Madeira wine . .	„	1134·1
Sparkling Sillery .	„	1462·8
Jamaica rum . .	„	1831·9

It is remarked by Graham that the flow of a liquid is greatly retarded by the presence of a small quantity of a soluble colloïd; so much so that the transpiration tube may be used as a colloïdoscope. The transpirability of different salts appear also generally to follow their ratio of diffusibility in water.

The isolated fact discovered by Poiseuille that aqueous alcohol has a point of maximum retardation, coincident with the degree of dilution at which the greatest condensation of the mixed liquids occurs,—which degree of dilution corresponds with the hydrate, $C^2H^6O.3H^2O$, has been made by Graham the starting-point of an important series of experiments on the relation between capillary transpiration and chemical composition. The 3-atom hydrate of methylic alcohol, $CH^4O.3H^2O$, though not distinguished by any particular degree of condensation in volume, exhibits a peculiarity in its transpiration rate, similar to that of dilute ethylic alcohol. The hydrated acids also, in many cases, exhibit a characteristic retardation of transpiration at a particular degree of hydration. In hydrated substances generally, the extent to which transpiration is affected by annexation of water, is by no means in proportion to the intensity of combination. In sulphuric acid, for instance, the maximum transpiration-time occurs with the hydrate $H^2SO^4.H^2O$; in acetic acid, with the compound $C^2H^4O^2.H^2O$; of nitric acid with $2HNO^3.3H^2O$; and with alcohol, as above observed, with the hydrate $C^2H^6O.3H^2O$. The transpiration-times of these hydrates are given, amongst other results, in the following table, in which the transpiration-time of water at the same temperature is taken as the unit of comparison:

Transpiration-times of Acids, Alcohols, and Ethers. (Graham.)

Liquid (undiluted).		Transpiration-time.	Degree of hydration.	Transpiration-time.
Water		1·0000		
Methylic alcohol	$C\ H^4O$	0·6300	+ $3H^2O$	1·8021
Ethylic alcohol	C^2H^6O	1·1950	+ $3H^2O$	2·7582
Amylic alcohol	$C^5H^{12}O$	3·6490		
Formate of ethyl	$C^3H^6O^2$	0·5110		
Acetate of ethyl	$C^4H^8O^2$	0·5530		
Butyrate of ethyl	$C^6H^{12}O^2$	0·7500		
Valerate of ethyl	$C^7H^{14}O^2$	0·8270		
Acetic acid	$C^2H^4O^2$	1·2801	+ H^2O	2·7400
Butyric acid	$C^4H^8O^2$	1·5650	+ H^2O	3·2790
Valerianic acid	$C^5H^{10}O^2$	2·1550	+ H^2O	3·8390
Nitric acid	NHO^3	0·9899	+ $\frac{3}{2}H^2O$	2·1034
Sulphuric acid	SH^2O^4	21·6514	+ H^2O	23·7706
Acetone	C^3H^6O	0·4010	+ $6H^2O$	1·6040

On comparing the transpiration-times of the several alcohols, ethers, and acids in this table, it will be seen that, so far as these observations extend, the order of succession of individual substances in any homologous series is indicated by their degree of transpirability as clearly as by their comparative volatility, the heaviest molecules having the slowest rate of efflux. It may also be observed that the transpiration rate of an acid is slower than that of an ether with which it is metameric; butyric acid, for example, is slower than acetate of ethyl.

LIQUORICE. See GLYCYRRHIZIN (ii. 920).

LIRIODENDRIN. A neutral substance, existing, according to Emmet, in the stem of the tulip-tree (*Liriodendron tulipifera*). It is obtained by exhausting the bark with water, concentrating to one-fifth, washing the impure substance which separates with weak potash, and crystallising from boiling dilute alcohol. It crystallises in scales or in radiating needles. It is bitter, melts at 83°, is partly volatile, sparingly soluble in water, very soluble in alcohol and ether. It is decomposed by strong hydrochloric or sulphuric acid, the latter converting it into a brown resin. Iodine colours it yellow.

LIROCONITE. *Octahedral Arsenate of Copper, Chalcophacite, Linsenerz.*—This mineral occurs in trimetric crystals, exhibiting the combination $\infty P . \bar{P}\infty$, occasionally an inch in diameter, but usually minute. Angle $\infty P : \infty P = 119° 20'$; $\bar{P}\infty : \bar{P}\infty = 72° 22'$. Cleavage lateral, but obtained with difficulty. Rarely granular. Hardness = 2 to 2·5. Specific gravity = 2·882 to 2·985. Lustre vitreous, inclining to resinous. Colour and streak sky-blue. Fracture imperfectly conchoïdal, uneven. Imperfectly sectile.

When heated it turns green and begins to glow, then becoming dark brown. On charcoal before the blow-pipe it melts slowly, and forms a red brittle bead; when reduced with carbonate of sodium, it yields white scales of arsenide of copper (Damour). It is completely dissolved by acids, and even by ammonia.

The following are analyses of liroconite from Cornwall; *a.* by Hermann (J. pr. Chem. xxxiii. 296)—*b.* by Damour (Ann. Ch. Phys. [3] xiii. 404)—*c.* by Trolle Wachtmeister (Kongl. Vet. Acad. Förhandl. 1832, p. 80):—

	As^2O^5	P^2O^5	Cu^2O	Al^4O^3	H^2O		
a.	23·05	3·73	36·38	10·85	25·01	=	99·02
b.	22·40	3·24	37·40	10·09	25·44	=	98·57
c.	23·14	2·98	39·16	8·94	25·78	=	100·00

These results may be represented by the following formulæ:

a. $(4Al^4O^3.P^2O^5).3(5Cu^2O.As^2O^5).48H^2O$
b. $(4Al^4O^3.P^2O^5).4(5Cu^2O.As^2O^5).60H^2O$
c. $(4Al^4O^3.P^2O^5).5(5Cu^2O.As^2O^5).72H^2O$

Liroconite occurs, with various ores of copper, pyrites, and quartz, at Huel Gorland and Huel Unity, in Cornwall; also in minute crystals at Herrengrund in Hungary, and in Voigtland. (Dana, ii. 429.)

LITHEOSPORE. Syn. with HEAVY SPAR.

LITHIUM. *Atomic weight* 7, *Symbol*, Li.—Lithia, the oxide of this metal, was discovered by Arfvedson in 1817. It was first obtained from petalite (silicate of aluminium and lithium), in which it exists to the amount of 5 per cent.; it exists also in lithia-spodumene (8 per cent.), amblygonite (11 per cent.), triphyline (3·4 per cent.), lepidolite (3·6 per cent.), apyrite, and the tourmaline of Uton in Sweden. The most abundant source of lithium yet discovered is a mineral spring in Cornwall, analysed by W. A. Miller (*Reports of the British Association*, 1864). In smaller quantities it is very widely diffused, being found in sea-water, in many micas and felspars, in the ash of various kinds of tobacco, in sea-water, and in many mineral springs.—Bunsen has lately detected it in the meteorite of Juvenas in France, and in that of Parnallee in South Hindostan (Ann. Ch. Pharm. cxx. 253), and Engelbach has found it in the metorite of the Cape. (Pogg. Ann. cxvi. 512.)

Brandes (Scherer's Annalen, viii. 120) stated that a white combustible metal is obtained from lithia by the action of the electric current, but metallic lithium was first obtained in definite form by Bunsen (Pogg. Ann. xciv. 107). The process is as follows:

Pure chloride of lithium is fused over a spirit-lamp in a small porcelain crucible, and decomposed by a zinc-carbon battery of 4 to 6 cells. The positive pole is a small splinter of gas coke (the hard carbon deposited in gas-retorts), and the negative pole an iron wire about the thickness of a knitting-needle. After a few seconds, a small silver-white regulus is formed under the fused chloride, round the iron wire and adhering to it, and after two or three minutes attains the size of a small pea. To obtain the metal, the wire pole and regulus are lifted out of the fused mass, by a small, flat, spoon-shaped iron spatula. The wire may then be withdrawn from the still melted metal, which is protected from oxidation by a coating of chloride of lithium. The metal may now be easily removed from the spatula with a pen-knife, after having been cooled under rock-oil. These operations may be repeated every three minutes; and thus an ounce of the chloride may be reduced in a very short time.

Lithium, on a freshly-cut surface, has the colour of silver, but quickly tarnishes on exposure to the air, becoming slightly yellow. It melts at 180°, and if pressed at that temperature between two glass plates, exhibits the colour and brightness of polished silver. It is harder than potassium or sodium, but softer than lead, and may, like that metal, be drawn out into wire. It tears much more easily than a lead wire of the same dimensions. It may be welded by pressure at ordinary temperatures. It floats on rock-oil, and is the lightest of all known solids, its specific gravity being 0·589—0·578. (Bunsen.)

Lithium is much less oxidable than potassium or sodium. It makes a lead-grey streak on paper. It ignites at a temperature much higher than its melting point, burning quietly, and with an intense white light. It burns when heated in oxygen, chlorine, bromine, iodine, or carbonic anhydride, and with great brilliancy on boiling sulphur. When thrown on water, it oxidises, but does not fuse like sodium. Nitric acid acts on it so violently that it melts and often takes fire. Strong sulphuric acid attacks it slowly; dilute sulphuric acid and hydrochloric acid quickly. Silica, glass, and porcelain are attacked by lithium at temperatures below 200°. (Bunsen, Ann. Ch. Pharm. xciv. 107.)

LITHIUM, CHLORIDE OF. LiCl. Produced when lithium burns in chlorine gas; also by dissolving lithia or carbonate of lithium in hydrochloric acid. By evaporating the aqueous solution at temperatures above 15·5°, or an alcoholic solution over sulphuric acid, the anhydrous chloride is obtained in cubes having the taste of common salt (C. Gmelin). According to Troost, it crystallises in regular octahedrons. According to H. Rose, it is more volatile than chloride of potassium, less volatile than chloride of sodium. In open vessels it volatilises even below a red heat, and is partially converted into carbonate.

The *hydrated chloride*, $LiCl.H^2O$ according to Rammelsberg, $LiCl.2H^2O$ according to Hermann and Troost, is formed when the anhydrous chloride deliquesces in the air, or when the aqueous solution is evaporated at a rather low temperature (below 10°), and crystallises in large rectangular prisms with four-sided summits resting on the lateral edges: it is probably isomorphous with hydrated chloride of sodium. By rapid crystallisation, it forms needles grouped in feathery tufts like sal-ammoniac (Hermann). Both the anhydrous and the hydrated chloride deliquesce rapidly in the air, and dissolve very readily in water and in alcohol. (C. Gmelin.)

LITHIUM, DETECTION AND ESTIMATION OF. 1. *Reactions in the dry way.*—Lithium salts are white, excepting those which contain a coloured acid, such as chromic acid. They are more readily fusible than the corresponding salts of potassium and sodium, and are permanent in the fire, if the acid is not too volatile or easily decomposed. Fused with *carbonate of sodium* on platinum foil, they cause a dark yellow stain round the circumference, whilst carbonate of sodium by itself produces this effect to a much smaller degree only (Berzelius). Fused on platinum wire they colour the blowpipe flame carmine-red. An excess of a potassium-salt does not interfere with the production of this colour, but the presence of a small quantity of soda gives rise to the yellow flame (H. Rose). Alcohol, in which a salt of lithium is dissolved or diffused in the state of fine powder, also burns with a carmine-red flame (C. Gmelin). The same occurs also with paper saturated with a solution of a salt of lithium, or the wick of a taper saturated with moistened phosphate or acetate of lithium (Turner, Ed. Phil. J. of Sc. ii. 267; iv. 113). By means of the spectroscope, the occurrence of very minute traces of lithium may be detected, by a brilliant crimson band, having a refrangibility between those of the lines B and C of the solar spectrum, and a faint yellow band somewhat less refrangible than the line D. In these two lines the whole light of the lithium spectrum is contained, when formed by the gas-flame of a Bunsen's burner. At very high temperatures, however, such as that of a hydrogen-flame, a blue line also makes its appearance.

2. *Reactions in Solution.*—All salts of lithium are soluble in water; but the carbonate and phosphate, and the double phosphate of lithium and sodium are but slightly soluble. Hence the other salts of lithium, when not dissolved in too much water, yield difficultly soluble precipitates with *carbonate of ammonium, potassium*, or *sodium*, and with *phosphate of sodium*. *Carbonate of sodium* precipitates the salts of lithium after some time only. Common *disodic phosphate* does not precipitate them in the cold, even after a long time, except on the addition of ammonia, which gradually gives rise to an abundant precipitate. But a mixture of a salt of lithium with phosphate of sodium becomes turbid by boiling or evaporation, and the dry residue, on being treated with water, leaves the difficultly soluble phosphate of lithium and sodium. *Phosphate of potassium* gives no precipitate, even on boiling or evaporation; but on the addition of *ammonia*, an abundant precipitate after some time (H. Rose). *Hydrofluosilicic acid* throws down from salts of lithium the almost insoluble fluoride of silicium and lithium (Berzelius), and *picric acid* precipitates picrate of lithium (H. Rose). Solutions of lithium-salts, even when concentrated, are not precipitated by perchloric acid, sulphate of aluminium, dichloride of platinum, oxalic acid, or tartaric acid.

A solution of a salt, which is not clouded by caustic soda in the cold, or by carbonate of sodium at a boiling heat, but yields with phosphate of sodium, on evaporation, an almost insoluble white powder, contains lithia. (Berzelius.)

3. *Quantitative Estimation and Separation.*—Lithium, after separation from other metals, may be estimated as carbonate, sulphate, or chloride. The hydrate and the organic salts of lithium are converted into carbonate, Li^2CO^3, when ignited in contact with the air. All lithium-salts containing volatile acids, may be converted into sulphate by heating them with sulphuric acid: the excess of acid may be expelled by simple ignition, without addition of carbonate of ammonia, because lithium does not form an acid sulphate. The chloride is not so well adapted for quantitative estimation as the sulphate, on account of its hygroscopic qualities; but as lithium is generally obtained as chloride, in the process of separating it from sodium, it is convenient to estimate it directly in this form: it must be ignited in a well-covered crucible, and weighed immediately after cooling.

Lithium may also be estimated as phosphate, Li^3PO^4, by evaporating the solution of a lithium-salt with phosphate of sodium, adding a quantity of hydrate or carbonate of sodium sufficient to keep the liquid alkaline; digesting the residue with ammonia, and washing the precipitate with a mixture of equal volumes of water and ammonia, then drying at 100°, and igniting. The determination may be rendered more exact by repeatedly evaporating the filtrate and wash-water, and treating the small quantities of lithium-phosphate thereby separated, as before (W. Mayer, Ann. Ch. Pharm. xcviii. 193; Jahresb. 1856, p. 739). According to Rammelsberg (Pogg. Ann. cii.

441; Jahresb. 1857, p. 141), solutions of lithium treated with phosphate and carbonate of sodium yield salts of the form M^3PO^4, containing variable quantities of lithium and sodium; but **Fresenius** (Zeitschr. Annal. Chem. i. 42) finds that the precipitate obtained as above always has the composition Li^3PO^4, and, accordingly, that Mayer's process is capable of yielding correct results.

Lithium is separated from the **earth-metals** and **heavy metals** in the same manner as the other alkalis, namely, by sulphydric acid, sulphide of ammonium, or carbonate of ammonium, &c. From **potassium** it may be separated by *dichloride of platinum*, which precipitates potassium, but not lithium; and from **sodium**, by converting the two alkalis into chlorides, and treating the dried chlorides, in a well closed bottle, with a mixture of *ether* and *absolute alcohol*, which, in the course of a few days, dissolves the chloride of lithium, and leaves the chloride of sodium.

As, however, this last process is somewhat tedious, and is apt to be rendered inexact by the presence of moisture, **Bunsen** (Ann. Ch. Pharm. cxxii. 348) recommends the following indirect method of estimating lithium, when it exists in the state of mixture or combination with other alkali-metals. The anhydrous mixture of the chlorides of the alkali-metals is repeatedly exhausted with ether-alcohol; the residue obtained by evaporating this solution is again treated in the same manner; and the evaporated residue of this extract is ignited and weighed. It is then dissolved in water; the total amount of chlorine is determined by precipitation with nitrate of silver; the filtrate is then freed from excess of silver by hydrochloric acid, and the potassium contained in it is precipitated by chloride of platinum. The quantity of chloride of potassium thus determined gives, when deducted from the total weight of the chlorides, a remainder $A = x$ chloride of lithium $+ y$ chloride of sodium; and the quantity of chloride of silver equivalent to the known quantity of chloride of potassium, gives, when deducted from the total weight of the chloride of silver, a weight B, whence the quantity of chloride of lithium is calculated by the formula—

$$x = 1{\cdot}0823\,B - 2{\cdot}6525\,A.$$

*4. *Atomic weight of Lithium.* The earlier determinations of this number by Arfvedson, Vauquelin, C. G. Gmelin, and Kralovansky, were much too high, having been made with lithium-salts containing sodium. Hermann, Berzelius, and Hagen, prepared carbonate of lithium free from sodium by precipitation with carbonate of ammonium, and converted it into sulphate, which was then analysed by precipitation with baryta. In this manner Berzelius obtained the number 6·5. The numbers obtained by Hermann and Hagen were lower, and even that of Berzelius has been shown by subsequent experiments to be too low, the error probably arising from partial decomposition of the carbonate of lithium during fusion.

Mallet (Sill. Am. J. xxii. 349), by decomposing chloride of lithium with nitrate of silver, obtained the numbers 6·92 and 6·96. **Diehl** (Ann. Ch. Pharm. cxxi. 93), by the analysis of carbonate of lithium, the purity of which had been tested by spectral analysis, found the atomic weight of the metal = 7·026. **Troost** (*ibid.* cxxiii. 384), by decomposing the pure carbonate with silicic acid, obtained the number 7·01; the analysis of the chloride gave the same result; and the decomposition of the carbonate by sulphuric acid yielded the number 7·06. From all these results, the number 7 is adopted as the true atomic weight of lithium.

LITHIUM, FLUORIDE OF. This compound crystallises from the aqueous solution in very small opaque grains, which, at the temperature of commencing redness, fuse to a clear mass, again becoming cloudy as it solidifies. It is very slightly soluble in water. (**Berzelius.**)

LITHIUM, OXIDE OF. *Lithia*, Li^2O.—*Anhydrous lithia* is obtained as a yellowish-white spongy mass, containing a certain quantity of peroxide, by burning lithium in oxygen, and leaving the product to cool in a stream of the gas. (**Troost**, Ann. Ch. Phys. [3] li. 703.)

The *hydrate* may be obtained from petalite, spodumene, or lepidolite, which are silicates containing lithium (most advantageously from lepidolite), or from triphyline, which is a phosphate of lithium, manganese, iron and aluminium, by the following processes:—

1. Lepidolite, petalite, or lithia-spodumene, reduced to fine powder by careful levigation, is ignited with twice its weight of quicklime; the mass is treated with hydrochloric acid, then with sulphuric acid; the resulting sulphate of lithium is dissolved out from the sulphate of calcium; and the last traces of calcium are removed by precipitation with oxalate of ammonium. The solution of sulphate of lithium is then treated with a quantity of baryta-water just sufficient to throw down the sulphuric acid, and the filtrate on evaporation yields hydrate of lithium.

2. **Troost** (Ann. Ch. Phys. [3] li. 121) heats 10 pts. of finely-powdered lepidolite

with 10 pts. of carbonate of barium, 5 pts. sulphate of barium, and 3 pts. sulphate of potassium. The fused mass separates on cooling into a heavy transparent glass and a supernatant white crystalline slag, consisting of the sulphates of barium, lithium, potassium, and sodium, and containing nearly all the lithium. The alkaline sulphates are dissolved out by water, and converted into chlorides by chloride of barium; the potassium is precipitated by chloride of platinum, and the chlorides of lithium and sodium are separated by means of alcohol and ether. In operating on a large scale, the double sulphate of lithium and potassium may be separated by fractional crystallisation.

3. Triphyline is dissolved in strong hydrochloric acid, nitric acid being added to bring the iron to the state of ferric oxide; the solution is evaporated to dryness; and the residue is treated with water, which leaves all the iron as insoluble phosphate. The solution containing the chlorides of lithium and manganese and a little phosphoric acid, is treated with sulphide of barium, which removes the two latter substances; the excess of barium is removed by sulphuric acid (or better, by carbonate of ammonium), and the filtrate is evaporated to dryness and ignited. Chloride of lithium thus obtained frequently contains chloride of sodium, which may be separated by alcohol and ether. The chloride is then converted into sulphate, and from this salt caustic lithia is obtained as above. (Müller, Ann. Ch. Phys. [3] xlv. 350.)

Hydrate of Lithium, LiHO, separates from the aqueous solution in small crystalline grains. It has the same taste, causticity, and alkaline action on vegetable colours as potash and soda, but is much less soluble in water. It melts easily below redness, forming a fused mass which has a crystalline fracture. It does not appear to volatilise at a white heat.

Fused lithia, as commonly prepared, corrodes platinum vessels powerfully, so that silver vessels should always be used for heating it. This action upon platinum is said, indeed, to be one of the best indications of the presence of lithium; but, according to Troost (Ann. Ch. Pharm. cxxiii. 384), it is not produced by pure lithia, or by any pure lithium-salt, but only by such as contain cæsium and rubidium.

Peroxide of Lithium is said by Troost to be formed, together with lithia, when lithium is burned in oxygen gas.

LITHIUM, SULPHIDE OF. Li^2S. This compound is formed when lithium is thrown on melted sulphur; also when sulphate of lithium is heated to redness with charcoal. It dissolves in water and alcohol more easily than lithia.

LITHOGRAPHY. See PRINTING, CHEMICAL.

LITHOMARGE. *Stone-marrow* (*Steinmark*). A kind of clay, of which there are two varieties, the friable and the indurated.

Friable Lithomarge.—Colour white. Massive and sometimes in crusts; particles scaly and feebly glimmering; streak shining. Slightly cohering. Soils slightly. Feels rather greasy; adheres to the tongue. Light. Phosphoresces in the dark. Its constituents are, according to Klaproth, silica 32, alumina 26·5, iron 21, chloride of sodium 1·5, and water 17·0. It occurs sometimes in tin-stone veins.

Indurated Lithomarge. Colours yellowish and reddish-white. Massive and amygdaloïdal. Dull, opaque. Fracture fine earthy. Streak shiny. Soft, sectile, and easily frangible; adheres strongly to the tongue; greasy to the touch. Specific gravity 2·44. Infusible before the blowpipe. Some varieties phosphoresce, and others, when moistened, afford an agreeable smell like that of nuts. Its constituents are, silica 45·25, alumina 36·5, oxide of iron 2·75, water 14, and a trace of potash (Klaproth). It occurs in veins in porphyry, gneiss, &c., at Rochlitz in Saxony, and at Zöblitz. (Jameson.)

LITHOSPERMUM. The root-bark of *Lithospermum arvense* contains a red colouring matter, which reacts with water, alcohol, ether, and alkalis, in the same way as that of alkanet (i. 128), excepting that the lithosperm-red forms a blue solution with ether, whereas alkanet-red forms a dark red solution. (Ludwig and Kromayer, Rép. Chim. app. 1859, p. 211.)

LITMUS. *Lackmus. Tournesol en pains.*—A blue colouring matter, used chiefly for preparing test-papers. It is obtained from various species of *Roccella*, *Variolaria*, and *Lecanora*, the same lichens in fact that yield archil (i. 355). It appears from the experiments of Gélis (Revue Scient. vi. 50) that the blue colouring matter is developed in the lichens by fermentation, when the proximate principles contained in them are metamorphosed in presence of an alkaline carbonate. Under the influence of the air and ammonia alone, these lichens yield nothing but archil; but if an alkaline carbonate is likewise present, the lichens undergo a totally different alteration, and the product of the fermentation, instead of being red or violet, has then a pure blue colour. This blue coloration is due to the combination of the new colouring matter with the alkali: for acids, as is well known, redden litmus, that is to say, they unite with the alkali, and liberate the colouring matter of the litmus, which in this state is red, like that of archil. When 2 pts. of *Roccella tinctoria* and 1 pt. carbonate of potassium are repeatedly moistened with carbonate of ammonium, or with urine which is saturated with that salt, the mass acquires in three days a brown or dirty red colour; in 20 or 25 days a purple red; in 30 days a blue colour; and in 40 days yields litmus of the finest colour (Gélis, J. Pharm. xxiv. 277). Litmus is prepared in Holland from *Lecanora tartarea* and *Roccella tinctoria* from the Canary Isles, the coloured mass obtained as above being thickened with chalk or gypsum.

Our knowledge of the colouring matters of litmus is not very exact, but they are probably derived directly from orcin, like orceïn, the colouring principle of archil. The principal of these colouring matters is azolitmin, and three others have been distinguished, namely, Spaniolitmin, erythrolein, and erythrolitmin. The following mode of preparation of these colouring matters is given by Kane (Phil. Trans. 1840, p. 298):

a. Commercial litmus in powder is exhausted with boiling water, and the pale blue residue, which contains the greater part of the colouring matter, is made up into a thin paste with water, and hydrochloric acid is added till effervescence ceases and the liquid exhibits a strong alkaline reaction. The mass is then thrown on a filter; and the residue, after being freed from excess of acid by washing with water, is well dried and repeatedly boiled with alcohol, as long as that liquid extracts anything from it. The alcoholic solution is evaporated to dryness over the water-bath, and the residue digested with warm ether as long as the ether is coloured by it. The ethereal solution, distilled in the water-bath to remove the ether, leaves Erythrolein in the form of a purple semi-fluid oil. The portion of the alcoholic extract which is insoluble in ether consists of Erythrolitmin.

The red-brown powder which remains after the boiling with alcohol (*vid. sup.*) consists of impure Azolitmin. This substance is either boiled with pure water, and pure azolitmin obtained by evaporating the strongly coloured solution; — or the residue insoluble in alcohol is boiled with ammoniacal water, and the blue solution evaporated to dryness, during which operation the greater part of the ammonia escapes; the remainder is separated by moistening the mass with hydrochloric acid, and washing the resulting sal-ammoniac with alcohol.

b. The strongly coloured liquid obtained by boiling litmus with water is precipitated with neutral acetate of lead; the precipitate washed with water, treated while still moist with sulphydric acid, and suspended in warm ammoniacal water; the dark blue liquid is evaporated to dryness, and moistened with hydrochloric acid; and the sal-ammoniac is separated by means of warm alcohol. The residue is but of small amount in proportion to the deep colour of the solution; it sometimes consists of pure azolitmin, more rarely of Spaniolitmin, a substance not containing nitrogen.

Azolitmin is a red-brown amorphous powder which dissolves with blue colour in ammonia, and forms blue and violet lakes.

Spaniolitmin has only been obtained mixed with azolitmin, but it appears to be of a light red colour.

Erythrolein is a semi-fluid mass of a fine red colour, and dissolves in ammonia, forming a purple liquid.

Erythrolitmin forms crystalline grains of a fine deep red colour, coloured blue by potash, and forming, with ammonia, a blue compound insoluble in water.

The following are the analytical results obtained by Kane with these substances, and calculated with the old atomic weight of carbon (6·12 or 12·24):

	Erythrolein.	Erythrolitmin.		Azolitmin.		Spaniolitmin.
Carbon . .	74·27	55·78	55·3	49·50	50·05	44·54
Hydrogen .	10·68	8·69	8·1	5·35	5·52	3·11

Of these four substances, azolitmin is the only one which contains nitrogen. Kane determined the nitrogen only by the comparative method which gave proportions of $N : CO^2$ varying from 1 : 17·3 to 1 : 18·3.

The composition of azolitmin approaches pretty nearly to the formula $C^7H^7NO^4$ (carbon 49·6, hydrogen 4·1, nitrogen 8·2), according to which azolitmin would contain 1 at. oxygen more than orceïn, and might be derived from orcin in the manner shown by the equation,

$$C^7H^8O^2 + NH^3 + O^3 = C^7H^7NO^4 + H^2O.$$

If this be true, the action of the alkaline carbonates in the formation of litmus may be explained by supposing that these salts accelerate the absorption of oxygen by orcin subjected to the influence of air and ammonia, so as to produce a new compound more highly oxygenated than orceïn.

The ammoniacal solution of azolitmin forms with the salts of the heavy metals, precipitates which are red or blue, according to the quantity of metal contained in them. The azolitmates of *barium* and *calcium* are blue. The *lead-compound*, which has a fine violet colour when recently prepared, but becomes blue when dried at 120°, appears to contain $2C^7H^6PbNO^4.Pb^2O$. The *stannous salt* is a lake of a fine violet colour; by exposure to the air in the moist state it is converted into a *stannic* compound of a splendid scarlet colour.

Azolitmin suspended in water through which chlorine gas is passed yields yellow chlorazolitmin.

Azolitmin subjected to the action of nascent hydrogen, is dissolved, and converted into a compound called by Kane, leucazolitmin, which, however, cannot be obtained pure, because it oxidises immediately and becomes coloured when exposed to the air. A white compound of leucazolitmin with stannic oxide is formed by boiling the stannous compound of azolitmin with water; on exposure to the air, it is immediately converted into the scarlet stannic compound of azolitmin.

LIVER, GLYCOGENIC FUNCTION OF. See Glycogen (ii. 906).

LIVER OF SULPHUR. An old term applied to a mixture of the higher sulphides of potassium, obtained by heating sulphur with carbonate of potassium in a covered vessel. (See Potassium, Sulphides of.)

LIXIVIATION. The application of water to the fixed residues of bodies, for the purpose of extracting the saline part.

LIXIVIUM. A solution obtained by lixiviation.

LOADSTONE. Magnetic iron ore (p. 397): see also Magnetism.

LOAM. See Clay (i. 1023).

LOBELINE. An alkaloïd existing, according to Bastick and Procter (Pharm. J. Trans. x. 270, 456) in *Lobelia inflata*. It is oily; cannot be volatilised without decomposition; dissolves very readily in water, alcohol, and ether; and forms crystallisable salts with hydrochloric, sulphuric, nitric, and oxalic acids. The solutions are precipitated by tannin. It acts as a narcotic when taken internally.

LOBOITE. A magnesian vesuvian from Norway. (See Vesuvian.)

LŒLINGITE. Syn. with Leucopyrite (p. 585).

LŒWEITE. A sulphate of magnesium and sodium, $MgNaSO^4.1\frac{1}{4}H^2O$, from Ischl, approaching astrachanite in composition. It is of yellowish colour, specific gravity 2·376, and gives by analysis 52·35 SO^3, 12·78 Mg^2O, 18·97 Na^2O, 14·45 H^2O, and 0·66 Fe^4O^3 and Al^4O^3 = 99·21. (Karafiat, Haid. Ber. 1846, p. 266.)

LOGANITE. A variety of pyrosclerite from Calumet Island on the Ottawa, Canada, where it occurs associated with serpentine, phlogopite, pyrites, and apatite, in crystalline limestone. It has a weak subresinous lustre, pale or dark brownish colour, and greyish streak. Hardness = 3. Specific gravity = 2·6—2·64. Sometimes in crystals with rounded angles, which appear to be pseudomorphs; one gave the angle 124°, near that of hornblende. Contains 32·49 per cent. silica, 13·18 alumina, 35·77 magnesia, 0·95 lime, 2·14 protoxide of iron, and 16·92 water (including carbonic acid) = 101·45. (T. S. Hunt, Phil. Mag. [4] ii. 65.)

LOGWOOD. *Bois de Campêche. Blauholz.*—The tree which yields this wood is called by Linnæus, *Hæmatoxylum campechianum*.

Logwood is so heavy as to sink in water, hard, compact, of a fine grain, capable of being polished, and scarcely susceptible of decay. Its predominant colour is red, tinged with orange, yellow, and black.

It yields its colour both to spirituous and watery solvents. Alcohol extracts it more readily and copiously than water. The colour of its dye is a fine red, inclining a little to violet or purple, which is principally observable in its watery decoction. This, left to itself, becomes in time yellowish, and at length black. Acids turn it yellow; alkalis deepen its colour, and give it a purple or violet hue.

Stuffs would take only a slight and fading colour from decoction of logwood, if they were not previously prepared with alum and tartar. A little alum is also added to the bath. By these means they acquire a pretty good violet.

A blue colour may be obtained from logwood, by mixing verdigris with the bath, and dipping the cloth till it has acquired the proper shade.

The great consumption of logwood is for blacks, to which it gives a lustre and velvety cast, and for greys of certain shades. It is also of very extensive use for different compound colours, which it would be difficult to obtain of equal beauty and variety by means of drugs affording a more permanent dye.

Decoction of logwood is frequently mixed with that of brazil-wood, to render colours deeper, their proportion being varied according to the shade desired.

Logwood is used for dyeing silk violet. For this, the silk must be scoured, alumed, and washed; because, without aluming, it would take only a reddish tinge that would not stand wetting. To dye silk thus, it must be turned in a cold decoction of logwood till it has acquired the proper colour; if the decoction were used hot, the colour would be in stripes and uneven.

Bergmann observed, that a fine violet might be produced from logwood by impregnating the silk with solution of tin. In fact we may thus obtain, particularly by mixing logwood and brazil-wood in various proportions, a great number of fine shades, more or less inclined to red, from lilac to violet. See Hæmatoxylin (p. 4). U.

LOMONITE. Syn. with Laumontite (p. 472).

LONCHIDITE. A variety of marcasite or white iron pyrites, found at Freiberg, Schneeberg, and in Cornwall. Hardness = 6·5. Specific gravity = 4·925—5. Colour, tin-white, sometimes greenish or greyish. Streak, black. According to Plattner's analysis, it contains 49·61 per cent. S, 4·40 As, 44·23 Fe, 0·35 Co, 0·75 Cu, and 0·20 Pb (= 99·24). (Breithaupt and Plattner, Pogg. Ann. lxxvii. 135.)

LOPEZ-ROOT. The root of *Toddalia aculeata.* By successive treatment with ether, alcohol, water, and dilute hydrochloric acid, it yields about 40 per cent. of soluble matter, consisting of a bitter principle, a tasteless resin, gum, tannin, starch, and oxalate of calcium. (H. Weber, Jahresber. 1859, p. 572. See also Schnitzer, *ibid.* 1862, p. 525.)

LOPHINE. $C^{21}H^{16}N^2$. *Pyrobenzoline.* (Laurent, Ann. Ch. Phys. [3] xix. 369. —Fownes, Ann. Ch. Pharm. liv. 365 and 368.—Gössmann, *ibid.* xciii. 331.— Gössmann and Atkinson, *ibid.* xcvii. 283; Chem. Soc. J. ix. 220.—Gm. xii. 199. —Gerh. iii. 179; iv. 1010.)—An organic base produced by the dry distillation of hydrobenzamide, benzoylazotide, or azosulphide of benzylene (Laurent), of amarine (Fownes), and by heating sulphite of benzoyl and ammonium with slaked lime (Gössmann). Its formation from hydrobenzamide (p. 183), or from the isomeric compound amarine, may be represented by the equation,

$$\underset{\text{Hydrobenzamide.}}{4C^{21}H^{18}N^2} = \underset{\text{Lophine.}}{3C^{21}H^{16}N^2} + \underset{\text{Oil.}}{C^{21}H^{18}} + 2NH^3.$$

The compound $C^{21}H^{18} = 3C^7H^6$ (polymeric with stilbene) is probably the oily matter which distils over with the lophine. (Gerhardt.)

Preparation.—1. When hydrobenzamide is heated, ammonia escapes, together with a mobile fragrant oil, and there remains a fused mass which may be distilled at a high temperature, but is more advantageously treated by pouring it out, pulverising it when cold, and digesting it in hot ether, which extracts a small quantity of a body crystallising in shining laminæ as the solution cools. The residue is heated with alcohol to the boiling point, and hot caustic potash added to it till the whole is dissolved; the liquid on cooling deposits thread-like crystals which may be washed with alcohol. It is better, however, to boil the residue insoluble in ether, with alcohol containing hydrochloric acid, mix the solution at the boiling heat with ammonia, and leave it to cool (Laurent).—2. From the mixture of lophine and amarine obtained by distilling benzoylazotide, the amarine is extracted by boiling with rock-oil, or the lophine by boiling with alcohol containing hydrochloric acid (Laurent).—3. From the distillate obtained by heating azosulphide of benzylene, the oily products are extracted by ether, the stilbene by boiling alcohol, and the thionessal by rock-oil, and the residue, consisting of lophine, is dissolved by boiling with alcohol and potash, or with alcohol containing hydrochloric acid. A similar process is adopted with the product resulting from distilling the mixture obtained by treating bitter-almond oil for two or three weeks with sulphydrate of ammonium, which mixture also contains picril (Laurent). —4. The needle-shaped crystals which sublime in the neck of the retort during the distillation of sulphite of benzoyl and ammonium with hydrate of calcium, are dissolved in hot alcohol, and recrystallised after being treated with animal charcoal. The formation of the lophine is facilitated by heating the retort very quickly and covering the upper part, at the commencement of the distillation, with red-hot coals (Gössmann). The best mode of conducting the process is to add a quantity of quicklime, equal in weight to the hydrate, introduce the mixture into a rather shallow globular retort coated with clay, and cover the retort, as far as it is filled with the mixture, with live coals, from the very beginning of the operation. Only small quantities should be operated on at once, from 10 to 15 grms. of the benzoyl-compound, with about 4 to 6 times the quantity of the lime mixture. When the operation is thus conducted, only a small quantity of amarine forms at first; and when this has melted down, the upper part of the retort begins to be covered with radiant masses of lophine, and the formation of secondary products ceases, nothing being formed but lophine and free ammonia. At the commencement, a small quantity of an aromatic oil accompanies the lophine, apparently resulting from the decomposition of the amarine into lophine and other products, the principal of which is amarone (Gössmann and Atkinson). Purification as in Laurent's method (1).

Properties.—Lophine forms colourless needles, often an inch long, grouped in tufts, and having a lustre similar to that of caffeine; they become opalescent after a while, but retain their lustre. At 250° the compound sublimes, gradually but completely, without previous fusion, and without decomposition. It melts at 265°, forming a transparent liquid, which at 260° solidifies in a radiating crystalline mass. It is tasteless and inodorous, with scarcely any alkaline reaction. The alcoholic solution exhibits fluorescence like quinine, but not in so high a degree. It has no action upon polarised light (Gössmann and Atkinson). G. Kühn (Chem. Centr. 1861, p. 237) obtained, by the dry distillation of hydrochlorate of hydrobenzamide (p. 184), two modifications of lophine, one crystallising in needles which melted at 230°, the other (likewise obtained by Ekman, Ann. Ch. Pharm. cxii. 151) in needles which melted at 170°.

The composition of lophine has been variously represented by the formulæ $C^{22}H^{17}N^2$ and $C^{22}H^{16}N^2$ (Laurent), $C^{21}H^{16}N^2$ (Fownes), $C^{21}H^{17}N^2$ (Gössmann and Atkinson), $C^{22}H^{16}N^2$ (Liszt). Fownes's formula, $C^{21}H^{16}N^2$, agrees best, on the whole, with the analyses, and likewise affords the best representation of the formation of the compound from hydrobenzamide (or from amarine):

	Calculation.		Laurent.		Fownes.	Gössmann.	Gössmann and Atkinson.
C^{21}	252	85·1	85·6	86·0	85·2	85·7	84·7
H^{16}	16	5·4	5·4	5·1	5·4	5·5	5·6
N^2	28	9·5	9·2	. .	9·1	. .	9·5
$C^{21}H^{16}N^2$	296	100·0	100·2		99·7		99·8

Laurent's second analysis, which differs considerably from all the rest, was probably made with impure material.

Lophine is insoluble in *water*, very sparingly soluble in boiling *alcohol* and *ether*, crystallising in needles on cooling. It dissolves to about the same amount in *rock-oil*, and in *oil of turpentine*, whence it separates in a crystalline powder on cooling. It dissolves easily and without decomposition in boiling *alcoholic potash*. (Laurent.)

According to Ekman (Ann. Ch. Pharm. cxii. 151), 100 pts. of absolute alcohol at 19° dissolve 0·81 pt. of lophine, and at 21° from 0·84 to 0·91 pt.; at the boiling point, 2·70 to 2·75 pts.; and 100 pts. ether dissolve 0·26 pt. lophine at 19°, 0·32 to 0·33 at 20°, and 0·32 at 21°. Of an indifferent substance, having nearly the composition of lophine, and formed, together with the latter, by the decomposition of hydrochlorate of hydrobenzamide at 160°–200° (p. 183), 100 pts. absolute alcohol dissolve 0·07 pt. at 16°, and 0·33 to 0·37 pt. at the boiling point; and 100 pts. ether at the boiling point dissolve 0·69 to 0·74 pt. of the same substance.

Decompositions.—Lophine boiled with *nitric acid* forms nitrolophine (Laurent). It is dissolved by *bromine*, without evolution of vapours of hydrobromic acid. When the mass is dissolved in ether, and the solution mixed with alcohol and abandoned to spontaneous evaporation, beautiful yellow prisms with rectangular base separate out; these crystals give off bromine when heated, and, when water is poured upon them, turn white and fall to powder (Laurent). Lophine in contact with *iodide of ethyl* does not form any substitution-compound, not even when the two bodies are heated together to 100° in a sealed tube for several weeks. A portion of the iodide of ethyl is decomposed into alcohol and hydriodic acid, which combines with the lophine. (Gössmann and Atkinson.)

The lophine-salts are for the most part insoluble in water, and sparingly soluble in alcohol.—They are rather unstable, having a tendency when recrystallised to give up part of their acid and form basic compounds; this is particularly the case with the sulphate. (Gössmann and Atkinson.)

Hydriodate of Lophine, $C^{21}H^{16}N^2.HI$, is prepared like the hydrochlorate, and crystallises readily in large needles, which are more soluble in alcohol and ether than the hydrochlorate. From a very acid solution, it separates in granular crystals. It dissolves very easily in iodide of ethyl. In other respects it resembles the hydrochlorate. (Gössmann and Atkinson.)

Hydrochlorate of Lophine, $C^{21}H^{16}N^2.HCl$, separates quickly on cooling from a solution of lophine in boiling alcohol containing hydrochloric acid. If a solution in a sufficient quantity of boiling alcohol be mixed with such a quantity of hot water that no immediate precipitate is formed, the liquid on cooling yields well defined crystalline laminæ (Laurent). The second modification of lophine, obtained by Kühn (p. 184), forms a hydrochlorate, also containing $C^{21}H^{16}N^2.HCl$, which crystallises in interlaced needles, melting at 160°. When hydrochloric acid is added to a hot saturated alcoholic solution of lophine till the mixture exhibits a decided acid reaction, the hydrochlorate separates on cooling in large transparent needles very much like the crystals of pure lophine. If left for some time in the mother-liquor, they change into small white opaque prisms, an alteration which is probably due to loss of water. Several other lophine-compounds exhibit a similar change. When lophine is treated with strong hydrochloric acid, it becomes resinous, and can only be restored to the crystalline state by removing the acid and crystallising from alcohol (Gössmann and Atkinson). The hydrochlorate is nearly insoluble in water, but dissolves pretty easily in alcohol (Laurent). It has a slight acid reaction, dissolves more readily in water and alcohol than the pure base, and exhibits stronger fluorescence. (Gössmann and Atkinson.)

Hydrochlorate of lophine unites with *dichloride of platinum* when the solutions of the two salts in boiling alcohol are mixed together, the double salt separating, as the liquid cools, in orange-coloured crystals, the formula of which is probably $C^{21}H^{16}N^2.HCl.PtCl^2$. The chloroplatinate of Kühn's second modification of lophine contains water of crystallisation, the amount of which was found to be different in different preparations.

Nitrate of Lophine, $C^{21}H^{16}N^2.HNO^3$, forms fine light laminæ, devoid of lustre. When heated till they soften, they give off 1 at. water (Laurent). From a concentrated alcoholic solution of lophine acidulated with nitric acid, the salt crystallises in small plates, which, if covered with strong nitric acid free from nitrous acid, are converted into an oily mass. (Gössmann and Atkinson.)

Sulphate of Lophine is obtained in small shining rectangular laminæ, by heating lophine with alcoholic sulphuric acid, and mixing the solution with hot water, whereupon crystallisation ensues. The alcoholic solution reddens litmus and is precipitated by water, a portion however remaining in solution, so that, on adding ammonia, a precipitate of lophine is still obtained. Laurent found in the dry salt 11·5 and 13·2 per cent. of sulphuric acid; the neutral salt requires 11·21 per cent. of sulphuric acid (Laurent). When a solution of lophine to which excess of sulphuric acid has been added is left to evaporate slowly, the sulphate separates in broad transparent tables, which become opaque and effloresce on exposure to the air. When crystallised more rapidly, the compound separates in large needles, which, if left for some time in the mother-liquor, change into small white opaque needles. At each crystallisation, the salt becomes more basic, and by frequent solution and recrystallisation, the acid may be almost entirely removed. (Gössmann and Atkinson.)

Lophine also forms crystalline compounds with *nitrate of silver* and *dichloride of platinum.*

LOTALITE. Syn. with Hornblende.

LOXOCLASE. A name applied by Breithaupt to a variety of felspar closely resembling orthoclase, if not identical with it.

LUBRICANTS. Oleaginous or fatty bodies used for reducing the friction between parts of a machine or carriage. (See *Ure's Dictionary of Arts, &c.* ii. 736; the chapter on Railway and Waggon Grease in *Richardson and Watts's Chemical Technology*, vol. i. pt. 3, p. 742; and the article Paraffin Oils in this Dictionary.)

LUCIFER MATCHES. See *Ure's Dictionary of Arts, &c.* ii. 737; *Richardson and Watts's Chemical Technology*, vol. i. pt. 4, p. 131; and the article Phosphorus in this Dictionary.

LUCULLITE. See Limestone, (p. 698).

LUMACHELLA. See Limestone, (p. 697).

LUNA CORNEA. Chloride of silver (see Silver).

LUNAR CAUSTIC. Nitrate of silver fused at a low heat (see Nitrates).

LUPININ. A bitter non-nitrogenous substance obtained from lupine-seeds. (Cassolu, Ann. Ch. Pharm. xiii. 308.)

LUPULIN. The yellow, granular, aromatic powder situated at the base of the cones of the hop, and forming from 8 to 18 per cent. of the cones. It contains five different substances; viz. a volatile oil, a resin, a nitrogenous substance, a bitter principle, and a gummy substance. The cones contain about 2 per cent. of the volatile oil. This oil and the resin probably give to beer its agreeable aromatic odour, while the bitter substance tends to preserve it. (See Hop, p. 165.)

LUPUS METALLORUM. The alchemical name of trisulphide of antimony.

LUTE. The lutes with which the joinings of vessels are closed are of different kinds according to the nature of the operations to be performed, and of the substances to be distilled in these vessels.

When vapours of watery liquors, and such as are not corrosive, are to be retained, it is sufficient to surround the joining of the receiver to the nose of the alembic, or of the retort, with slips of paper or of linen covered with flour-paste. In such cases also, slips of wet bladder may be conveniently used.

When more penetrating and dissolving vapours are to be retained, a lute is to be employed of quicklime slacked in the air, and beaten into a liquid paste with whites of eggs. This paste is to be spread upon linen slips, which are to be applied exactly to the joining of the vessels. This lute is very convenient, dries easily, becomes solid, and sufficiently firm. Vessels may be formed of it hard enough to bear polishing on the wheel.

Lastly, when acid and corrosive vapours are to be retained, we must have recourse to the lute called *fat lute*. This lute is made by forming into a paste some dried clay finely powdered, sifted through a silken sieve, and moistened with water, then beating this paste well in a mortar with boiled linseed oil, that is, oil which has been rendered drying by litharge dissolved in it, and fit for the use of painters. This lute easily takes and retains the form given to it. It is generally rolled into cylinders of a convenient size. These are to be applied, by flattening them, to the joinings of the vessels, which ought to be perfectly dry, because the least moisture would prevent the lute from adhering. When the joinings are well closed with this fat lute, the whole is to be covered with slips of linen spread with lute of lime and whites of eggs. These slips are to be fastened with packthread. The second lute is necessary to keep on the fat lute, because this latter remains soft, and does not become solid enough to stick on alone.

Gutta percha may be united to glass, in tube apparatus, by fusing the gutta percha at the point of junction by means of a hot iron knife-blade.

Fine porcelain clay, mixed with a solution of borax, is well adapted to iron vessels, the part received into an aperture being smeared with it. U.

LUTEOLIN. The yellow colouring matter of weld (*Reseda luteola*). It was first isolated by Chevreul (J. Chim. méd. vi. 157), and has been more fully examined and analysed by Moldenhauer (Ann. Ch. Pharm. c. 180) and by Schützenberger and Paraf (*ibid.* Suppl. i. 139). Moldenhauer prepares it by exhausting weld with alcohol, distilling off the alcohol from the extract; then washing with water and drying the residue; exhausting it with ether; dissolving the residue left on evaporating the ethereal solution in alcohol; adding a larger quantity of water; heating to the boiling point; filtering hot; and leaving the filtrate to cool. The product may be purified by recrystallisation from boiling very dilute spirit containing 1 or 2 per cent. alcohol. Schützenberger and Paraf exhaust the plant with alcohol, precipitate the extract with water, and heat the precipitate with water to 250° in a steel apparatus; the luteolin then crystallises on the sides of the vessel on cooling, and may be purified by two crystallisations from superheated water.

Luteolin crystallises from solution in boiling dilute alcohol, also from a hot saturated solution in dilute sulphuric or acetic acid, in yellow four-sided needles arranged in radiate groups; it may also be obtained in needles by careful sublimation. It melts at 320° with partial decomposition, to a black-brown mass. It is inodorous, has a slightly bitter, astringent taste; dissolves in 14,000 pts. of cold and 5,000 pts. of boiling *water*, in 37 pts. *alcohol* [at what temperature?] and in 625 pts. of *ether*. It reddens litmus paper slightly, and unites with *metallic oxides*. It dissolves with deep yellow colour in *caustic alkalis* and *alkaline carbonates*, remaining in the pure state when its ammoniacal solution is evaporated (Moldenhauer). By prolonged heating with *ammonia*, it is completely dissolved, forming a deep yellow solution, and leaving on evaporation a dark coloured residue which gives off ammonia when heated with potash (Schützenberger and Paraf). In cold dilute *acids* it is but sparingly soluble; more easily in cold *concentrated sulphuric acid*, forming a yellow solution from which it is separated by water without alteration. It dissolves sparingly in cold concentrated *hydrochloric acid*, more easily in warm concentrated *nitric acid*, but is nearly insoluble in that acid when cold. Dilute *nitric acid* acts upon it only when heated; strong nitric acid dissolves it with deep red colour, the solution being decolorised by prolonged boiling, with formation of oxalic acid (Moldenhauer). Heated to 200° with *phosphoric anhydride*, it yields a red substance which dissolves with violet colour in ammonia (Schützenberger and Paraf). Distilled with *chromate of potassium* and *sulphuric acid*, it yields formic acid. It does not precipitate a solution of *gelatin*, but forms a green precipitate with a very dilute solution of *ferric chloride*, and colours a concentrated solution brown-red (Moldenhauer). According to Chevreul, the aqueous extract of weld forms beautiful yellow precipitates with *alum*, *stannous chloride*, and *acetate of lead*, a blackish-grey precipitate with *ferrous sulphate*, and brown with *sulphate of copper*.

According to Moldenhauer, luteolin contains 62·5 to 63·0 per cent. carbon and 3·70 to 4·1 hydrogen, whence he deduces the formula $C^{20}H^{14}O^{8}$, requiring 62·8 C, 3·7 H, and 33·5 O. According to Schützenberger and Paraf, the air-dried substance heated to 150° gives off 10·23 per cent. water, and that which has been dried over sulphuric acid gives off 7·02 per cent. at the same temperature. Luteolin dried at 150° gave by analysis 61·6 to 62·5 per cent. carbon, and 3·5 to 3·8 hydrogen, whence Schützenberger and Paraf deduce the formula $C^{12}H^{8}O^{5}$, which requires 62·1 C, 3·4 H, and 34·5 O. To the substance dried over sulphuric acid, they assign the formula $C^{12}H^{10}O^{6}$, and to the air-dried substance, $2C^{12}H^{10}O^{6}.H^{2}O$. A *lead-salt* precipitated from the alcoholic solution of luteolin by alcoholic acetate of lead, gave by analysis 30·97 per cent. C, 1·98 H, and 49·33 $Pb^{2}O$, agreeing nearly with the formula $C^{12}H^{8}O^{5}.Pb^{2}O$, which requires 31·65 C, 1·76 H, 17·58 O, and 49·0 $Pb^{2}O$.

LUTIDINE. $C^{7}H^{9}N$. An organic base isomeric with benzylamine or toluidine (i. 575), discovered by Anderson (Ann. Ch. Pharm. lxxx. v.) in bone-oil. This oil contains a number of oily bases soluble in hydrochloric acid; and on decomposing the resulting solution with potash and rectifying, lutidine passes over at about 145°. The same base is found in coal-tar naphtha and in shale naphtha, the liquid obtained by distilling the bituminous shale of Dorsetshire (Gr. Williams, Chem. Soc. J. vii. 97); also among the volatile bases obtained by the distillation of peat. (Vohl, Jahresb. 1859, p. 742. Church and Owen, Phil. Mag. [4] xx. 110; Jahresber. 1860, p. 359.)

A base isomeric, but not identical with that from bone-oil, occurs among the products of the dry distillation of cinchonine, and passes over in rectification between 160° and 166°. Greville Williams, who discovered this base (i. 869), and has recently instituted a searching comparison between its properties and that of Anderson's base (Proc. Roy. Soc. xiii. 305), distinguishes it as β-lutidine. The properties of the two bases and of many of their salts are essentially different, as will be seen by the following comparative statements.

Physical properties of the Bases.—Both bases when pure are colourless refractive oils, lutidine having a density of 0·9467 at 0°, and β-lutidine of 0·9555 at the same temperature. Lutidine boils at 154°; β-lutidine betwen 163° and 168°. Vapour-density of lutidine, by experiment (at 200°) = 3·839 (Anderson); of β-lutidine (at 213°) = 3·787 (Williams); by calculation = 3·699. It may be inferred from this that the boiling point of β-lutidine has not been estimated above the truth, because if the fraction had been taken too high, the vapour-density would have erred in excess.

Lutidine has a most characteristic smell, resembling that of its lower homologues, but less pungent, and more approaching the aromatic; this odour is never altered in the least by any method of purification, and after boiling with nitric, chromic, or any other acid, it is still given off on neutralisation with an alkali. All the salts, however purified, emit the same smell on the addition of an alkali. *β-lutidine* has also a most characteristic smell, quite unlike that of lutidine, and somewhat resembling that of nicotine, but with out the peculiar pungency of that base, and far more pleasant. No treatment with acids, or oxidising agents, and no amount of purification of its salts, makes the least alteration in the smell, or causes it to approach, however distantly, to that of lutidine.

Lutidine dissolves readily when shaken with three or four times its bulk of water, and on warming the liquid, it becomes milky, the base separating from it. *β-lutidine*, on the contrary, requires not less than 25 parts of water to dissolve it, and the solution does not become turbid when warmed; on the contrary, a mixture of water and lutidine, cloudy from excess of base, becomes clear on warming. Hence it appears that lutidine is less, β-lutidine more soluble in hot than in cold water.

Both lutidine and β-lutidine unite with *acids* and with *salts*, forming crystalline compounds, most of which are very soluble.

Compound of β-lutidine with Cupric Sulphate. $(C^{7}H^{9}N)^{2}Cu^{2}SO^{4}.4H^{2}O$.—When β-lutidine is gradually added to a solution of cupric sulphate, a copious pale green precipitate is formed, which dissolves in excess, forming a rich blue liquid, which after filtration, soon becomes filled with brilliant blue prisms of considerable size, and having in the air-dried state the composition above given. They give off 2 at. water at 100°, and become anhydrous at 200°. (Williams.)

Gold-salts, $C^{7}H^{9}N.HCl.AuCl^{3}$.—Both bases give salts having this composition; but a mixture of hydrochlorate of *β-lutidine* with trichloride of gold became nearly solid, whereas with the *lutidine-salt* the precipitate occupied only half the bulk of the liquid, and did not require more than a fourth of the quantity of water to dissolve it that was necessary in the case of β-lutidine. (Williams.)

Mercuric salt of Lutidine, $C^7H^9N.2HgCl$, or $C^7H^9N.HhgCl^2$. This salt separates from a mixture of the alcoholic solutions of lutidine and mercuric chloride, as a white bulky precipitate; from dilute solutions it is gradually deposited in radiating crystals. It dissolves in boiling water, with partial decomposition; more freely, and without alteration, in boiling alcohol. (Anderson.)

Palladium-salts.—The chloropalladite of β-lutidine, $C^7H^9N.HCl.PdCl$, is obtained, as a nearly solid mass of garnet-red prisms, on leaving a mixture of the base, hydrochloric acid, and chloride of palladium, to itself for four days. When heated for a long time to 100°, it is decomposed, 1 at. hydrochloric acid being given off from 2 at. of the salt, and leaving the compound:

$$C^{14}H^{19}N^2Cl^3Pd^2 = (C^7H^9N.HCl.PdCl).C^7H^9NPd.Cl$$

The *chloride of palladio-β-lutidyl-ammonium*, $N\left\{\begin{matrix}(C^7H^9)'''\\ Pd\end{matrix}\right\}Cl$, the base existing in the last-mentioned substance, is easily obtained by acting on chloride of palladium in solution with β-lutidine. This base is not easily soluble, and precipitates at once. (Williams.)

On mixing solutions of hydrochlorate of *lutidine* and chloride of palladium, exactly similar in concentration to those above employed, no crystals were obtained by the time that the contents of the vessel containing the β-lutidine had nearly solidified: and even after a month's repose, the quantity obtained was much smaller than with β-lutidine.

Platinic salts.—The *chloroplatinates* of both bases have the composition $C^7H^9N.HCl.PtCl^2$, and crystallise in rectangular tablets; but the β-lutidine-salt exhibits the same superior facility of crystallising that is observed in the corresponding gold- and palladium-salts. The presence of hydrochloric acid in excess greatly retards the formation of the lutidine-salt (Anderson); but Williams finds that this is not the case with the β-lutidine-salt, a mixture of the hydrochlorate of β-lutidine with platinic chloride and a large excess of hydrochloric acid instantly becoming nearly solid.

Decomposition of the Platinic salts by boiling.—Chloroplatinate of β-lutidine begins to decompose the instant the solution enters into ebullition, an insoluble yellow powder beginning to deposit, and rapidly increasing in quantity. After boiling with water, this salt has the composition of *dihydrochlorate of platino-lutidine*, $\beta N\left\{\begin{matrix}C^7H^7\\ Pt''\end{matrix}\right\}2HCl$.

The solution of chloroplatinate of lutidine, on the other hand, required 2½ hours active boiling before any deposit began to form; and even after several hours' boiling, the deposit was very small.

Platinous salts.—When equal weights (1 grm. each) of platinous chloride and β-lutidine were mixed in an apparatus surrounded with a non-conducting medium, the temperature rose from 16° to 84°, and a hard brittle product was obtained, agreeing almost exactly in composition with the formula $C^7H^9N.PtCl$.—When lutidine was treated with platinous chloride under exactly the same conditions, the temperature rose two degrees higher; but the product, instead of becoming a hard brittle mass, remained of the consistence of treacle.

Substitution-derivatives of Lutidine.

Ethyl-β-lutidine.—A mixture of 1 vol. β-lutidine and 2 vol. iodide of ethyl heated in a sealed tube to 94° for three minutes, solidified on cooling to a mass of crystals of *iodide of ethyl-β-lutidine*, $C^7H^8(C^2H^5)N.HI$.—The *platinum-salt* prepared therefrom in the usual way, crystallises in superb orange-coloured fronds, containing $C^9H^{13}N.HCl.PtCl^2$. This salt when boiled with water turns black, and deposits platinum. After two days boiling, it yielded 27·5 per cent. of the metal, the original salt containing 28·99 per cent. (Gr. Williams.)

Ethyl-lutidine.—A mixture of lutidine and iodide of ethyl in the above proportions, heated to the same temperature for the same time, showed no signs of crystallisation on cooling. It required an hour's digestion to effect combination; and in twenty-four hours, only half the product had crystallised, the rest remaining in the form of a syrup. (Gr. Williams, Proc. Roy. Soc. xii. 311.)

Methyl-β-lutidine, $C^8H^{11}N = C^7H^8(CH^3)N$.—β-lutidine mixed with iodide of methyl, becomes heated, and forms *hydriodate of methyl-β-lutidine*, a salt very soluble in water and alcohol, but nearly insoluble in ether. Its alcoholic solution evaporated to a syrup, remains liquid if left at rest; but on touching it, beautiful long needles shoot through the liquid, which soon becomes completely solid. The *chloroplatinate*, $C^8H^{11}N.HCl.PtCl^2$, forms crystals containing 30·29 per cent. platinum. (Gr. Williams, Ed. Phil. Trans. xxi. [2] 317.)

LYCINE. (Husemann and Marmé, Ann. Ch. Pharm. Suppl. ii. 383.)—A base contained in the box-thorn (*Lycium barbarum*). The leaves are repeatedly boiled with water (the stems yield but a small product); the extracts are precipitated with basic acetate of lead; and the filtrate, freed from lead by sulphydric acid, and neutralised with carbonate of sodium, is evaporated to a third of its original volume. The liquid, very strongly acidulated with sulphuric acid, is then precipitated with a solution of phosphomolybdate of sodium, or a mixture of 30 at. tungstate and 1 at. phosphomolybdate. The light yellow precipitate, after washing with water acidulated with sulphuric acid, is mixed, while still moist, with carbonate of barium, dried over the water-bath, and exhausted with boiling alcohol. The extracts leave, after evaporation of the alcohol, a syrupy residue, from which the base may be dissolved out by dilute hydrochloric acid, while a resinous body remains undissolved. The hydrochlorate, which has a strong acid reaction, is easily soluble in water, sparingly in absolute alcohol, nearly insoluble in ether, and crystallises from alcohol in dazzling white rhombic prisms, sometimes half an inch long, and from water in fern-like groups of crystals. The free base, obtained by treating the hydrochlorate with carbonate of barium and alcohol, is a white, radio-crystalline, deliquescent mass, which has a sharp but not bitter taste, dissolves easily in water and alcohol, very sparingly in ether, and melts with decomposition when heated. Most of its salts are crystallisable, and easily soluble in water; some of them are also deliquescent.

LYCOPODIUM. The fine dust of lycopodium, or clubmoss, consists of the spores of the plant; when diffused or strewed in the air, it takes fire from a candle, and burns off like a flash of lightning. It is used in theatres.

From 1000 parts of these spores, Bucholz extracted 60 parts of a fixed oil soluble in alcohol, 30 of sugar, 15 of mucilage, 895 of a substance insoluble in water, alcohol, ether, essence of turpentine, and cold alkaline leys.

The leaves contain 5·0 per cent. chlorophyll, 25·0 extractive matter and acetate of aluminium, 6·0 organic salts of calcium, magnesium, manganese, iron, lead (?), and copper (?), and 64·0 cellulose.

The infusion of lycopodium is used as a mordant, on account of the large quantity of acetate of aluminium which it contains. (Pelouze et Frémy, *Traité*, vi. 469.)

LYDIAN STONE, *Touchstone*, or *Basanite*, a velvet-black siliceous stone or flinty jasper, used, on account of its hardness and black colour, for trying the purity of the precious metals. See GOLD (ii. 929).

LYMPH. This liquid, which fills the lymphatic vessels, is colourless or yellowish when pure, red only if blood-corpuscles happen to be mixed with it. It is sometimes transparent, sometimes slightly turbid or opalescent, of a faintly saline taste and mawkish animal odour; its reaction is usually alkaline. It coagulates in from four to twenty minutes after its discharge from the lymphatics, then forming a gelatinous, trembling, colourless coagulum, which gradually contracts more firmly, and encloses a large number of the so-called lymph-corpuscles: this coagulum usually occupies but a very small space in proportion to the serum.

The especial *morphological elements* of lymph, in addition to fat-globules and nucleus-like formations, are the true lymph-corpuscles, which, however, do not differ essentially from mucus- and pus-corpuscles. In lymph that has been carefully collected, blood-corpuscles are not found, excepting when the liquid has been obtained from the lymphatics of the spleen, or from animals that have been starved to death. (H. Nasse, *Handwört. d. Physiol.* ii. 363–410.)

The *chemical constituents of lymph* are in general similar to those of blood, without the red corpuscles. The spontaneously coagulating substance of the lymph is perfectly identical with the fibrin of blood. In human lymph (obtained in cases of disease or injury), Marchand and Colberg found 0·52 per cent. and L'Héritier 0·32 per cent. fibrin; while in the lymph of the horse, from 0·04 to 0·33 per cent. has been found by different observers. J. Müller found that frogs which had been starved to death during winter yielded a lymph perfectly free from fibrin; whereas Nasse found that the lymph of frogs which had been kept in a heated room still coagulated.

The albumin of the lymph has the same general properties as blood-albumin. Geiger and Schlossberger found, however, that albumin from the lymph of a horse, though it exhibited no reaction with vegetable colours, did not coagulate on boiling, but that, on evaporation, a membrane was formed on the surface of the liquid as if a strongly alkaline albuminate of sodium had been present. This lymph-serum was not rendered turbid by acetic acid, unless boiled after acidification: neither was it coagulated by rennet, whence the absence of casein may be inferred; nor by ether. In human lymph, the albumin has been found to vary from 0·434 to 6·002 per cent., and in that of the horse from 1·2 to 2·75 per cent. In the ash of lymph-albumin, even after repeated extraction with water and spirit, Nasse found an extraordinarily large quantity of alkaline carbonates.

Fat occurs in lymph only in small quantities, and for the most part in a saponified form; in the lymph of the horse, Nasse found 0·0088 per cent. of free fat, and 0·0575 per cent. of alkaline salts of fatty acids; while in human lymph, Marchand and Colberg found 0·264 per cent. of a pale reddish fat.

The lymph also contains lactates.

In horses' lymph, Nasse found 0·0755 per cent. of extractive matters soluble in alcohol, and 0·9877 per cent. soluble in water only; while, according to Geiger and Schlossberger, the whole of the extractive matters amount to 0·27 per cent. Nasse was unable to detect urea in the lymph of the horse.

Mineral constituents.—In lymph, as in all the animal fluids, chloride of sodium is the preponderating mineral constituent: in horses' lymph, it amounts, according to Nasse, to 0·4123 per cent. Alkaline carbonates were found by Nasse in horses' lymph, the quantity being estimated at 0·056 per cent.; but Geiger failed in detecting them: in the ash of the solid constituents of the lymph, however, the latter found an abundance of alkaline carbonates. The presence of ammoniacal salts, which was suspected by Nasse, has been definitely established in horses' lymph by Geiger and Schlossberger. Nasse found that horses' lymph is comparatively rich in sulphuric acid, which exists in it pre-formed; he estimates the quantity of sulphate of potassium at 0·0233 per cent. Alkaline phosphates occur only in very small quantities. The earthy salts, with a small quantity of ferric oxide (arising probably from the presence of a few blood-corpuscles), were found by Nasse to amount to only 0·031 per cent. in horses' lymph.

The quantity of water in lymph appears to be very variable, but never so great as in the blood-plasma. In human lymph, Marchand found 96·926 per cent. and L'Heritier found 92·436 per cent. water; in the lymph of horses, the quantity has been found to vary from 92·5 to 98·37 per cent.

Nasse has instituted an interesting comparison (based on direct analyses) between the composition of the lymph and of the blood-serum of the horse, from which it appears that the individual salts stand to one another in precisely the same ratio in the two liquids, although their absolute quantity is very different, on account of the comparatively larger proportion of water in the lymph.

There are also considerable differences in the proportions in which the mineral constituents stand to the organic matters in the two liquids: while 100 pts. of salts correspond to 1036 pts. of organic matters in the blood-serum, the ratio in the lymph is as 100 to only 785. According to Marchand and Colberg, human lymph contains organic and inorganic matters in nearly equal parts. (*Lehmann's Physiological Chemistry*, translated by Day, ii. 299.)

LYNCURION. A Greek name for AMBER.

M.

MACE is the *arillus* or envelope of the fruit of the nutmeg (*Myristica moschata*). It forms a somewhat thick, tough, unctuous, reticulated membrane, of a yellowish-brown or orange colour; has a somewhat more agreeable odour than nutmeg, with a warm and pungent taste, and is used as a condiment in cooking.

Mace contains two oils, one of which is unctuous, bland, and of the consistence of butter; the other, which is obtained by distillation with water, is thinner and volatile. By cohobating four times, 4·7 per cent. oil may be obtained (Hoffmann, Repert. Pharm. xliii. 296); from old mace, 4·1 per cent. (Bley, *ibid.* xlviii. 94). It is transparent and colourless; of specific gravity 0·931; smells strongly of mace, and has a burning aromatic taste. It forms a permanent liniment with aqueous ammonia.

MACLE is the name given to certain spots in minerals of a deeper hue than the rest; sometimes proceeding from difference of aggregation, sometimes from the presence of a foreign substance: clay-slate, for example, may be macled with iron pyrites.

MACLES. Twin-crystals (ii. 159).

MACLURIN. Syn. with MORINTANNIC ACID (p. 1049).

MADDER. *Garance. Krapp.*—The root of *Rubia tinctorum*, extensively used in dyeing for the production of a variety of colours, namely, red, pink, purple, black, and chocolate. Other species of *Rubia* yield similar colouring matters, and are also used as dyeing materials; viz. *R. Mungista*, or *Munjeet*, which grows in the mountainous regions of Hindoostan, and is used in that country for producing the red and chocolate figures seen in the chintz calicoes of the East Indies; and *R. peregrina*, which is cultivated in the Levant, where it is called *Alizari*, and imported into this country under the name of *Turkey-roots;* but *Rubia tinctorum*, or *dyers' madder*, is the only species cultivated in Europe: it thrives best in a warm climate, and is grown extensively near Avignon in France, also in Alsace and in Naples; in the north of Europe it requires a sheltered situation.

All kinds of madder have a peculiar smell, and a taste between bitter and sweet. Their colour varies extremely, being sometimes yellow, sometimes orange-red, reddish-brown, or brown. They are more or less hygroscopic; so that even when closely packed in casks in the state of powder, they slowly attract moisture, increase in weight, and at length lose their pulverulent condition, forming a firm coherent mass. Some kinds of madder, especially those of Alsace and Holland, when mixed with water and left to stand for a short time, give a thick coagulum or jelly—an effect which does not take place in the same degree with Avignon madder. The madder of Avignon contains so much carbonate of calcium as to effervesce with acids. The herbaceous parts of the plant, when given as fodder to cattle, are found to communicate a red colour to their bones.

The principal advantages which madder presents, as a dye-stuff, are the following:—1. It is capable of producing, according to the mordants and the method of treatment, a great variety of different colours and shades; such as black; red of different kinds, from a dull brownish red to a bright red and delicate pink, besides the peculiar colour known as Turkey-red: also purple of various shades, from a dull reddish-purple to a delicate bluish-purple or lilac, as well as chocolate of all shades.—2. Its colouring matters have but little affinity for cotton fibre, and a great affinity for mordants; so that it is not difficult to secure a good white on the parts of the tissue to which no mordant has been applied.—3. The compounds which its colouring matter or matters yield with mordants, possess an unusually stable character; so that they may be exposed, without much detriment to the colour, to the action of various agents for the purpose of improving or modifying the shade.

Chemical Constitution of Madder. There is probably no subject connected with the art of dyeing which has given rise to so much discussion as the composition of madder, and the chemical nature of the colouring matters to which it owes its valuable properties. The subject has engaged the attention of a great number of chemists, among whom may be especially mentioned, Robiquet and Colin, Kuhlmann, Gaulthier de Claubry and Persoz, Runge, Schunck, Schiel, Higgin, Debus, Strecker, Rochleder, Sacc, and Emile Kopp. Nevertheless, our knowledge of madder, as compared with that which we possess of other colouring principles, is still confused and uncertain. According to some chemists (Sacc, for example) and many manufacturers, madder contains but one colouring principle, while most others admit the existence of at least two, viz. alizarin and purpurin. Moreover, according to some chemists, the colouring matter exists in madder ready formed; whereas others suppose that fresh madder contains merely a colour-generating substance, which subsequently, by a kind of fermentation gives rise to the colouring matter properly so called: the latter, which is Schunck's view, appears to be based on the most trustworthy experiments.

When ordinary commercial madder is exhausted with boiling water, a dark-brown muddy liquid is obtained, having a taste between bitter and sweet. On adding a small quantity of an acid to this liquid, a dark-brown precipitate is produced; while the supernatant liquid becomes clear, and appears of a bright yellow colour. The precipitate consists of alizarin, purpurin, rubiacin, two resinous colouring matters, pectic acid, oxidised extractive matter, and a peculiar nitrogenous substance. The liquid filtered from this precipitate contains the bitter principle and the extractive matter of madder, as well as sugar, and salts of potassium, calcium, and magnesium. No starch, gum, or tannin can be detected in the watery extract. After the madder has been completely exhausted with boiling water, it appears of a dull-red colour. It still contains a quantity of colouring matter, which cannot, however, be extracted with hot water, or even by alkalis, since it exists in a state of combination with lime and other bases, forming compounds which are insoluble in those liquids. If, however, the residue be treated with boiling dilute hydrochloric acid, that acid dissolves a quantity of lime, magnesia, alumina, and sesquioxide of iron, as well as some phosphate and oxalate of calcium, which may be discovered in the filtered liquid; and if the remainder, after being well washed, be treated with caustic alkali, a dark-red liquid is obtained, which gives with acids a dark reddish-brown precipitate of alizarin, purpurin, rubiacin, resin, and pectic acid. The portion of the madder left after treatment with hot water, acids, and alkalis, consists almost entirely of woody fibre. (Schunck.)

Of the substances thus shown to exist in ordinary madder, the most important are undoubtedly alizarin and purpurin, which are in fact the essential red colouring matters of the dye-stuff. They were discovered by Robiquet and Colin, to whom we are indebted for the first memoir of any importance relating to the chemistry of madder. (Ann. Ch. Phys. [2] xxxiv. 225.)

Alizarin, the *Lizaric acid* of Debus, *Madder-red* of Runge, *Matière colorante rouge* of Gaulthier de Claubry and Persoz, was obtained by Robiquet and Colin as a sublimate, in beautiful reddish-yellow needles; but the mode of preparation which they adopted left it uncertain whether the alizarin pre-existed in madder, or was a product of decomposition of some other body produced by heat.

It may, however, be extracted from ordinary madder, as used by the dyer, by the action of solvents, and obtained in crystals without sublimation: hence its existence in ordinary madder may be inferred (see i. 114; and for details of preparation, *Gmelin's Handbook*, xiii. 326, and xiv. 130). Its composition cannot be regarded as definitely established. Wolff and Strecker's formula, $C^{10}H^6O^3$, is most in accordance with the relation of alizarin to chloronaphthalic acid, $C^{10}H^5ClO^3$, both of these compounds being converted, by the action of nitric acid, into phthalic acid; but Schunck's formula, $C^{14}H^{10}O^4$, appears to explain more clearly the formation of alizarin from rubian (p. 745): it must be remembered, however, that the formula of rubian itself is by no means well established. Alizarin is very little soluble in water, more soluble in alcohol, but nearly insoluble in aluminium-salts. Its alkaline solutions have a beautiful violet or purple colour, and it forms lakes of various colours with the earthy and heavy metallic oxides.

Purpurin, the *Madder-purple* of Runge, *Matière colorante rose* of Gaulthier de Claubry and Persoz, *Oxilizaric acid* of Debus, is extracted from madder by the same processes as alizarin, and separated from it by its superior solubility in alum-liquor. It bears considerable resemblance to alizarin, yielding a crystalline sublimate when heated, and being very sparingly soluble in water, but more soluble in alcohol. The properties by which it is distinguished from alizarin, are its easy solubility in boiling alum-liquor, forming a solution of a beautiful pink colour, with yellow fluorescence; and secondly, the colour of its alkaline solutions, which are cherry-red or bright red; whereas alizarin forms violet solutions with alkalis. These differences might, however, be produced by the admixture of some foreign substance with alizarin; and accordingly some chemists, as already observed, do not regard purpurin as a distinct substance, but attribute all the colouring power of madder to alizarin. There are, however, other characters which show beyond doubt that purpurin is a distinct substance: viz.—1. Its decomposition when exposed to the air in alkaline solution, the colour of the liquid then changing from bright red to reddish-yellow, and ultimately disappearing almost entirely, after which purpurin can no longer be discovered in the solution, whereas alizarin suffers no such decomposition (Schunck).—2. Its optical properties. Stokes has shown that when a solution of purpurin is examined by a prism, the spectrum which it exhibits is totally different from that which is produced in like manner by alizarin. (See LIGHT, p. 638; also PURPURIN.)

Considerable difference of opinion likewise exists as to the relative value of alizarin and purpurin as dyeing materials. According to Robiquet and Schunck, the finest and most permanent madder-colours are produced by alizarin; whereas Runge and Strecker are of opinion that the liveliest tints are produced by purpurin, and that this substance likewise plays the principal part in the manufacture of Turkey-red. According to E. Kopp, on the other hand, the real basis of Turkey-red is alizarin; and he further states that purpurin, though it dyes mordanted fabrics perfectly, does not yield colours of so great a degree of stability, and has not so great an affinity for oiled cloth, as alizarin.

From Schunck's experiments, it appears that all the usual madder-colours may be obtained by means of alizarin, and that the colours so produced are as pure and brilliant as ordinary madder-colours are after a long course of treatment with soap, acids, &c. They are likewise equally fast, and quite equal to ordinary madder-colours in their power of resisting decomposition by soap, alkalis, &c.

In short, the final result of dyeing with madder and its preparations appears to be simply the combination of alizarin with the various mordants employed. It can easily be shown, indeed, that the finer madder-colours contain little besides alizarin in combination with the mordant. If, for instance, a few yards of 'madder-pink calico' be treated with hydrochloric acid to remove the alumina of the mordant, then well washed and treated with caustic alkali, a violet solution is obtained from which acids precipitate yellow flocks consisting of almost pure alizarin. Purpurin, on the other hand, is found to have almost entirely disappeared from all madder-colours which have been subjected to a long course of after-treatment; a result quite in accordance with the fact above mentioned of the decomposition of purpurin in alkaline solution on exposure to the air. (Schunck.)

Madder likewise contains certain yellow colouring matters: but they are useless, if not positively injurious, in the process of dyeing. **Rubiacin** is a yellow crystallised colouring matter, coinciding in most of its properties with the *madder-orange* of Runge. It is only slightly soluble in boiling water, but dissolves more freely in boiling alcohol, and crystallises therefrom, on cooling, in greenish yellow lustrous scales and needles. It dissolves without decomposition in strong sulphuric and in boiling nitric acid, and with purple colour in alkalis. Its compounds with metallic oxides are mostly red. When treated with a boiling solution of ferric chloride or nitrate, it dissolves entirely, yielding a brownish-red solution, which gives with hydrochloric acid a flocculent precipitate of **rubiacic acid**.

Of the two resinous colouring matters already mentioned (p. 742), one is a dark-brown, brittle, resin-like body, very soluble in alcohol, and melting at a little above 100°; the other is a reddish-brown powder, less soluble in alcohol than the preceding. These two colouring matters, together with rubiacin, constitute probably the **tawny or dun colouring matter** of madder mentioned by the older chemists. They do not contribute to the intensity of the colours dyed with madder, and exert a very prejudicial effect on the beauty of the dyes. If printed calico be dyed with a mixture of alizarin and any one of these three colouring matters, the colours are found to be both weaker and less beautiful than when alizarin is used alone. The red acquires an orange tinge, and the purple a reddish hue, whilst the black is less intense, and the parts which should remain white have acquired a yellowish colour. The effect of these colouring matters must, therefore, be counteracted as much as possible by preventing them either from dissolving in the dye-bath, or from attaching themselves to the fabric.

The other organic constituents of madder are also for the most part injurious in dyeing. The **pectin**, in the state in which it exists in the root, is probably an indifferent substance; but, in consequence of the ease and rapidity with which it passes into pectic acid, it may act very prejudicially in dyeing, by combining with the mordants and preventing them from taking up the colouring matter.

The **extractive matter** of madder, when in an unaltered state, produces no injurious effects directly; but by the action of oxygen, especially at elevated temperatures, it acquires a brown colour, and then contributes, together with the rubiacin and resinous colouring matters, to deteriorate the colours, and sully the white parts of the fabric. Hence the uniform dirty reddish-brown tint which a piece of calico exhibits, both on the printed and unprinted portions, after having been dyed with madder; the removal of this tinge is one of the objects of the after-treatment with soap and other materials. In the process of manufacturing garancin, this substance is partly decomposed, partly removed by the subsequent washing: and this explains, in a great measure, the greater purity and brilliancy of garancin colours, as compared with madder colours. The extractive matter, when pure, has the appearance of a yellow syrup, like honey, is easily soluble in water and in alcohol, and is not precipitated from its aqueous solution by any earthy or metallic salt; but the solution, if evaporated in contact with the air, gradually turns brown, and then gives an abundant brown precipitate with acetate of lead. Its aqueous solution mixed with hydrochloric or sulphuric acid, and boiled, becomes green and deposits a dark-green powder. Hence this extractive matter has been called **chlorogenin** by Schunck, **rubichloric acid** by Rochleder. The **xanthin** of Kuhlmann and the **madder-yellow** of Runge appear to be mixtures of the extractive matter with a bitter principle.

The **sugar** contained in madder is probably glucose: it has not hitherto been obtained in the crystallised state; but it yields alcohol and carbonic acid by fermentation, like ordinary sugar. The **woody fibre** which remains after madder has been thoroughly exhausted by the action of various solvents (p. 742), always retains a slight reddish or brownish tinge, from the presence of some colouring matter which cannot be completely removed, and seems to adhere to it in the same way as it does to the fibre of unmordanted cotton.

The **inorganic constituents** of madder-root have been analysed by **H. Köchlin** (Ann. Ch. Pharm. lix. 344) and **K. Moy** (*ibid.* liv. 346); those of the seed by **Sehiel** (Handw. d. Chem. iv. 609).

	Ash of root.			
	From Alsace.		From Zealand.	
	a.	*b.*		Ash of Seed
Potash	29·35	26·64	3·42	20·08
Soda	15·89	11·67	25·76	6·20
Lime	34·54	29·25	16·29	29·89
Magnesia	3·72	3·68	3·17	2·48
Ferric oxide	1·18	3·36	2·67	3·74
Phosphoric anhydride	5·26	4·62	16·84	5·10
Sulphuric „	3·68	2·14	2·86	3·00
Silicic „	1·64	5·36	16·41	19·22
Chloride of sodium	4·71	13·25	12·58	10·29
	99·97	99·97	100·00	100·00

The Alsace madder (*a*) grown on a highly calcareous soil yielded 8·25 per cent. ash; *b* yielded 8·4 per cent. The seed of Avignon madder gave 8·14 per cent. ash.

Formation of the Red Colouring Matters.—The extraction of alizarin and purpurin from madder by the action of solvents shows that these colouring matters exist ready-formed in madder in its ordinary state, as used by the dyer. But it still remains a question whether they exist in the root while growing or when newly dug up, or whether they are formed by any subsequent process of chemical change. Now, it has long been known that when ground madder is kept tightly packed in casks, it constantly improves in quality for several years, after which it again deteriorates; and it was always supposed that this effect was due to some process of slow fermentation. The real nature of the change, however, remained for a long time unknown. Strecker supposes that the change which goes on consists in the conversion of alizarin into purpurin; but this would constitute anything but an improvement in quality, since the colours produced by purpurin are in most respects inferior to those of alizarin. Besides this, alizarin is a body not easily decomposed, unless exposed to the action of very potent agents; and any portion of it once formed in the root, would probably resist the action of air and moisture for a very long period of time, if not entirely. Mr. Higgin of Manchester states, as the results of his experiments on this subject, that there exists in madder a peculiar albuminous ferment, which, by acting on the xanthin, gives rise to the formation of colouring matter; and that this process takes place to some extent even during the short period of time occupied in dyeing. This view has been confirmed in its main features by the experiments of Schunck.

That the whole of the colouring matter of madder does not exist ready-formed in the article as used by the dyer, may be rendered evident by a simple experiment. If madder be exhausted with cold water, the clear watery extract does not contain any alizarin or other colouring matter, since these are almost insoluble in cold water. Nevertheless, the extract when gradually heated is found capable of dyeing in the same way as madder itself. If made tolerably strong, it possesses a deep yellow colour and a very bitter taste; but if it be allowed to stand in a warm place for a few hours, it gelatinises, and the insoluble jelly which is formed is found to possess the whole of the tinctorial power of the liquid, while the latter has lost its yellow colour and bitter taste. Hence it may be inferred that the substance which imparts to the extract its bitter taste and yellow colour, is capable of giving rise to the formation of a certain portion of colouring matter. By extracting madder with boiling water, the subsequent gelatinisation or coagulation is prevented, and the extract retains its yellow colour and bitter taste; a proof that the coagulation observed in the extract with cold water is a result of some process of chemical change which is arrested when the temperature is sufficiently raised. When the extract is agitated with a little animal charcoal, the latter absorbs the bitter principle, and gives it up again to boiling spirits of wine, which on evaporation leaves it in an almost perfect state of purity. In this manner Schunck obtained a substance to which he has given the name of Rubian, and of which the principal characteristics are these:—It is amorphous and shining like gum, has a deep yellow colour and an intensely bitter taste, is easily soluble in water and alcohol. It is not a colouring matter in the practical sense of the word, for it gives to mordants in dyeing only the faintest shades of colour. But if its watery solution be mixed with sulphuric acid and boiled, it gradually deposits a quantity of insoluble yellow flocks and becomes almost colourless. These flocks, after being well washed, are found to dye exactly the same colours as alizarin. In fact they contain alizarin. The liquid gives the reactions of sugar. Taking this fact into consideration, it becomes possible to give an account of the principal change which takes place in the process of manufacturing garancin. It is evident that during this process, the easily soluble rubian becomes converted into the difficultly soluble alizarin, that there is in this case, in fact, an actual formation of colouring matter which is added to that already existing in the root. A similar change takes place when caustic alkali is used in place of the acid. A solution of rubian on being mixed with caustic potash or soda, simply turns red, but on being boiled, it becomes dark purple and deposits a purple powder which consists chiefly of a compound of alizarin with alkali, insoluble in caustic lye. Fermentation also decomposes rubian with great facility; but in order to effect its decomposition it is not indifferent what ferment is taken: a peculiar ferment is essential to the purpose. A solution of rubian may be left for several days in contact with yeast, decomposing albumin, casein, emulsin, &c., without showing any sign of change. But if an extract of madder with cold water be mixed with a large excess of alcohol, flocks of a dirty red colour are precipitated, which, after being well washed with alcohol, are found to consist chiefly of an azotised principle called Erythrozym, which exerts a peculiar and powerful decomposing effect on rubian. If some of this substance be mixed with a watery solution of rubian, and the mixture be left to stand at the ordinary temperature, the rubian is found after a few hours to be as completely decomposed as if it had been treated with a strong acid or caustic alkali, though no evolution of gas or any of the usual signs of fermentation have been manifested. The solution, if tolerably strong, gelatinises just as an extract of madder with cold water does, under the same circumstances. The jelly, when mixed with cold water, is found to be almost insoluble. The water acquires only a slight colour, but contains sugar in solution, while the insoluble portion contains alizarin mixed with the ferment. This process of decomposition affords an explanation of the fact, well known to madder dyers, that if the dye-bath be heated up rapidly to the boiling point, instead of gradually, as is the usual practice, prejudicial effects ensue. In fact, the sudden heating puts a stop to the action of the ferment, as would be the case in any other process of fermentation, whereas the gradual heating allows it to exert its full decomposing power on the rubian. Hence, too, the advantage of mixing together several sorts of madder, one containing perhaps an excess of rubian in proportion to ferment, the other a superabundance of ferment to counterbalance it. The improvement which takes place in the quality of madder after long keeping is probably also an effect of the same cause. Indeed, it seems highly probable that the alizarin, which undoubtedly exists ready formed in ordinary madder, owes its formation to the action of fermentation on rubian; and an experiment made with fresh madder roots goes far to prove that this is in fact the case, and that the fresh root contains no trace of ready formed colouring matter. Some madder roots having been taken out of the ground and cut small, without being dried, produced the ordinary colours when used for dyeing in the common manner. But on treating the roots, after being cut into pieces as quickly as possible, with boiling alcohol, a yellow extract was obtained, which contained rubian, but which, even after all the alcohol had been driven away, was found incapable of imparting to mordants any but the slightest shades of colour; while the portion of the root left undissolved by the alcohol, on being subjected to the same test as the extract, imparted to mordants no more colour than the latter. It was evident, therefore, that the alcohol in this case had effected a separation between the colour-producing body and the agent which, under ordinary circumstances, is destined to effect its transformation into colouring matter. The same relation, it is apparent, subsists between rubian and erythrozym, as between amygdalin and emulsin.

Erythrozym differs in composition from all other known ferments, containing but a small proportion of nitrogen not exceeding 4 per cent. It acts on an aqueous solution of sugar nearly in the same manner as yeast, giving rise to the formation of alcohol, carbonic acid, hydrogen and succinic acid, but it is distinguished from all other ferments by its power of acting on rubian.

As rubian, when subjected to the action of acids, alkalis, or erythrozym yields alizarin and glucose, the decomposition might at first sight be supposed to consist simply in the resolution of the rubian into these compounds, according to the usual mode of decomposition of glucosides. The real decomposition is however much more complex, the products never consisting of alizarin and glucose only. The part insoluble in cold water contains in all cases, besides alizarin, two resinous colouring matters, namely, **Rubiretin**, $C^{14}H^{12}O^{4}$, easily soluble in alcohol, and **Verantin**, $C^{14}H^{10}O^{5}$, less soluble in that liquid. But in addition to these, there is uniformly found accompanying the alizarin, a third body, belonging, as far as general appearance and properties are concerned, to the same class of substances as rubiacin. The third body is, however, in each case quite distinct. When acids have been employed for the decomposition of rubian, then this third body is found to have the following properties:—It is tolerably soluble in boiling water, and crystallises in lemon-yellow silky needles; it is decomposed on being heated, but resists the action of nitric and concentrated sulphuric acids; this substance, **Rubianin**, contains, according to Schunck, $C^{22}H^{24}O^{10}$. When alkalis are used instead of acids, the rubianin is replaced by **Rubiadin**, $C^{16}H^{14}O^{5}$,* which is a body crystallising in beautiful golden-yellow scales, insoluble in water, but soluble in alcohol, and completely volatilised when heated. But when rubian is decomposed by fermentation, it yields neither of these two, but in their place **Rubiafin**, a substance agreeing in composition with rubiadin, and resembling it in most of its properties, but essentially distinguished from it by passing into rubiacic acid when treated with ferric chloride. This substance is usually accompanied by another of similar properties, called **Rubiagin**, of which it is difficult to say whether it must be considered as distinct from the others, since it has not been obtained in a state of perfect purity. All these bodies which accompany alizarin make their appearance so invariably under the circumstances above mentioned, that their occurrence cannot be considered as accidental.

Assuming for rubian the formula $C^{28}H^{34}O^{15}$, Schunck's view of the formation of these compounds may be represented in equations as follows:—

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* Schunck gives for rubiadin the formula, $C^{32}H^{13}O^{9}$; but this is improbable on account of the uneven numbers of hydrogen and oxygen atoms ($O = 8$)

a. Formation of alizarin ($\mathrm{C^{14}H^{10}O^{4}}$ according to Schunck):

$$\mathrm{C^{28}H^{34}O^{15} = 2C^{14}H^{10}O^{4} + 7H^{2}O.}$$

b. Of verantin and rubiretin:

$$\mathrm{C^{28}H^{34}O^{15} = C^{14}H^{10}O^{5} + C^{14}H^{12}O^{4} + 6H^{2}O.}$$

c. Of rubianin and glucose:

$$\mathrm{C^{28}H^{34}O^{15} + H^{2}O = C^{22}H^{24}O^{10} + C^{6}H^{12}O^{6}.}$$

d. Of rubiadin and rubiafin:

$$\mathrm{C^{28}H^{34}O^{15} + 2H^{2}O = C^{16}H^{14}O^{5} + 2C^{6}H^{12}O^{6}.}$$

Or rubiadin and rubiafin may be considered as products of the further metamorphosis of rubianin:—

$$\mathrm{C^{22}H^{24}O^{10} + H^{2}O = C^{16}H^{14}O^{5} + C^{6}H^{12}O^{6}.}$$

It appears, then, that rubian undergoes, not one, but three different processes of decomposition when acted on by acids, alkalis, or ferments; that the formation of sugar is connected not with that of alizarin, but with that of rubianin and its allies, and that in fact there is no reason why only one of these processes should not take place to the exclusion of the others; why, for instance, rubian should not be so decomposed as to yield alizarin alone, without any of the accompanying bodies, which are from this point of view, not only a source of loss, but also prejudicial in practice.

The formation of alizarin and of the other products of rubian above mentioned, does not depend upon oxidation. Nevertheless, according to Schunck, rubian does suffer a partial oxidation when its aqueous solution, mixed with an alkali or alkaline earth, is exposed to the air, the product formed being rubianic acid, $C^{52}H^{29}O^{27}$, (or perhaps $C^{52}H^{30}O^{28}$ = $\mathrm{C^{26}H^{30}O^{14}}$). Its formation may perhaps be represented by the equation:

$$\underset{\text{Rubian.}}{\mathrm{C^{28}H^{34}O^{15}}} + \mathrm{O^{5}} = \underset{\text{Rubianic acid.}}{\mathrm{C^{26}H^{30}O^{14}}} + \mathrm{2CO^{2} + 2H^{2}O.}$$

It is a true glucoside, and is resolved by the same agents which effect the decomposition of rubian into alizarin and glucose, no secondary products making their appearance; perhaps thus:

$$\underset{\text{Rubianic acid.}}{\mathrm{C^{26}H^{30}O^{14}}} + \mathrm{2H^{2}O} = \underset{\text{Alizarin.}}{\mathrm{C^{14}H^{10}O^{4}}} + \underset{\text{Glucose.}}{\mathrm{2C^{6}H^{12}O^{6}}}.$$

For further details respecting all these products, see RUBIAN.

Use of Madder in Dyeing. The chief use of madder is in cotton-dyeing and calico-printing. In woollen-dyeing it is not so much employed, especially in this country, only the ordinary woollen goods being dyed red with it; the colour is not so bright as that obtained with cochineal or lac, although more permanent and cheaper. Silk is seldom dyed with madder, because cochineal affords brighter tints.

The series of operations usually adopted for printed calicoes is as follows:—

1. The calico having been singed and bleached, the mordant is printed on; namely, '*red liquor*' (acetate of aluminium containing a small quantity of sulphate) for red or pink; '*iron liquor*' (ferrous acetate) for violet, purple, or black; and a mixture of this with *red-liquor* for chocolate.

2. The printed cloth is hung up with free access of air for about two days. During this process of "ageing," the mordant undergoes important changes, and becomes to a great extent insoluble, and therefore fixed in the cotton: *red-liquor* parts with a great part of its acetic acid, and its alumina remains as a highly basic sulphate; *iron-liquor* absorbs oxygen and loses acetic acid, and is thus converted into a basic ferric acetate. Of late years, a "rapid ageing process" has come into extensive use; it consists in passing the printed calico through a heated chamber, the atmosphere of which is kept exactly saturated with water-vapour. This process is frequently completed in about half an hour, but the time required for it, as well as for the ordinary ageing process, varies with the amount of mordant upon the cloth.

3. The next operation is called "dunging," and consists in passing the cloth through a hot mixture of cow-dung and water. During this process, superfluous portions of the mordant, which would otherwise get detached from the cloth during the dyeing and would be precipitated in combination with colouring matter upon the unprinted parts, are removed (perhaps in combination with organic constituents of the bath), and the remainder is converted more or less completely into phosphate. For a good many years past, the use of cow-dung in this process has been to a great extent superseded by that of an artificial preparation known as "dung substitute," first introduced by Mercer, the essential constituents of which are alkaline phosphates and arsenates. (See DYEING, ii. 353.)

4. Steeping in the madder-bath, which is kept lukewarm at first, and gradually raised to the boiling heat.

5. "Clearing," by passing the fabric through a boiling mixture of bran and water, or soap and water, or through a weak solution of chloride of lime, or by "crofting," that is, exposing it for some time on the grass to the action of air and light, or by several of these processes in succession.

To obtain greater variety of colours, other dye-stuffs are sometimes added to the madder-bath, *e. g.* quercitron or fustic for orange, logwood for blacks, &c.

For further details relating to the operations of madder-dyeing, see *Ure's Dictionary of Arts, &c.*, articles MADDER and TURKEY-RED.

The chemical changes which take place during the process, may be shortly described as follows: In the first place, the water of the dye-bath extracts the more soluble constituents of the madder, such as the sugar, extractive madder, and bitter principle (rubian). The latter is decomposed by the ferment, and the colouring matter thereby formed is added to that already existing in the root. As the temperature rises, the less soluble constituents, such as the alizarin, purpurin, rubiacin, resinous colouring matters, pectin and pectic acid, begin to dissolve, and at the same time combine partly with the mordants of the fabric, partly with the lime and other bases contained in the root, or added to the dye-bath, and thus permit the liquid to take up fresh quantities from the madder. The extractive matter acquires at the same time a brown colour by the combined action of heat and oxygen, and covers the white portions of a piece of printed calico with a uniform brown tinge. At the same time the alumina mordant has acquired a dirty brownish-red colour, and the iron mordant a black or brownish-purple, so that the fabric, after removal from the dye-bath, presents a very unsightly appearance. To clear the whites, and at the same time brighten the colours by removing the rubiacin, resinous matters, extractive matter, &c., and leave nothing but the alizarin combined with the mordants, is the object of the fifth operation or series of operations above-mentioned. But even this treatment, though sufficient for the more ordinary descriptions of goods, does not completely remove the foreign substances; for which reason the finer descriptions of printed calicoes are subjected to an after-treatment, which is as follows: "The goods, after being very fully dyed, generally with addition of chalk, and then washed, are passed for some time through a solution of soap, which is heated to a moderate temperature. By this means, a great deal of colour is removed, as may be seen by the red tinge of the soap-liquor, and the purity of the white portions is almost entirely restored. During this process, the brown and yellow colouring matters are probably removed by double decomposition, the alkali of the soap combining with and dissolving them, while the fat acid takes their place in the fabric. After being washed, the goods are passed through a weak solution of acid, mostly sulphuric or oxalic, or an acid tin-salt, which causes the colours to assume an orange tinge. The point at which the action of the acid liquid is to be arrested, can only be ascertained by practice. The next step in the process is, after washing the goods, to treat them again with soap-liquor in a close vessel under pressure. By exposing the goods on the grass for some time after the first soaping, the use of acid may be obviated; but the process then becomes much more tedious. In this way are produced those beautiful pinks and lilacs, which, for delicacy of hue, combined with great permanence, are not surpassed by any dyed colours known in the arts. Whether the fat acid of the soap employed forms an essential constituent of these colours, is not certainly known; but it is probable that it contributes to their beauty and durability. It is certain, however, that they always contain fat acid. If a piece of calico which has gone through the processes just described be treated with muriatic acid, the colour is destroyed, and a yellow stain is left in its place. This yellow stain disappears on treating the calico, after washing with water, with alkali, yielding a solution of a beautiful purple colour. This solution gives again, with an excess of acid, a yellow flocculent precipitate, which, after filtration, dissolves almost entirely in boiling alcohol, and the solution, on evaporation, affords needle-shaped crystals of pure alizarin, mixed with white masses of fat acid. The latter, therefore, seems to occupy the place taken up by the impurities before treatment with soap." (Schunck.)

An essential condition for the production of permanent madder-colours is the presence of a certain quantity of lime in the bath. This was first pointed out by Hausmann, who, after having produced very fine reds at Rouen, where the water is calcareous, encountered the greatest obstacles in dyeing the same reds at Logelbach near Colmar, where the water is nearly pure; but on adding chalk to his dye-bath, he obtained reds as beautiful and as permanent as those which he had formerly produced at Rouen. It has also long been known that Avignon madder, which is grown on a highly calcareous soil, and contains so much calcic carbonate as to effervesce with acids, affords the most permanent colours, whereas Alsace madder requires the addition of chalk in order to produce the same effect. The lime appears to act by uniting with those constituents of the madder (the rubiacin, pectic acid, &c.), which when taken up by the mordants in large quantity, act injuriously on the colour: for Schunck and

Robiquet have shown by experiment that, in dyeing with pure alizarin, the least addition of lime is rather injurious than otherwise, as it weakens the colours without adding to their durability. On the other hand, the addition of rubiacin, of the resinous colouring matters, or of pectic acid to alizarin was found to be very prejudicial, the red then acquiring an orange, and the purple a reddish hue, while the black became brownish, and the white parts of the fabric assumed a yellowish tinge: but these effects disappeared completely as soon as the foreign colouring matter was completely saturated with lime, the tinctorial power of the alizarin then reappearing with all its original intensity. Too great a quantity of lime must however be avoided, as it would take hold of the alizarin itself, and prevent it from uniting with the mordants.

Preparations of Madder. Since madder contains a variety of substances which impair the brightness and permanency of the colours produced by alizarin and purpurin, it follows that the process of dyeing with it must be greatly facilitated by the previous removal of these substances. This object is attained by treating madder with sulphuric acid, which destroys the rubiacin, resinous colouring matters, gum, pectin, extractive matter, &c., and at the same time, by its action on the rubian still existing in the madder, increases the quantity of alizarin and purpurin. Madder thus treated produces dyes which require less clearing than ordinary madder-colours; and there is this further advantage in its use, that nearly all the colouring matter contained in it is available for dyeing, whereas when crude madder is employed, nearly a third of the colouring matter remains in the residue unutilised. These considerations have led to the use of the following preparations of madder:

1. Sulphuric Charcoal (*Charbon sulphurique*).—This name was given by Robiquet to a product which he obtained by treating pulverised madder with a considerable quantity of rather strong sulphuric acid for several hours, then diluting with water, filtering, washing, and drying the residue. It dyes strongly and produces very fine colours; but being difficult and costly to prepare on the large scale, its manufacture has been abandoned, excepting for the preparation of colorin, a product introduced into commerce by MM. Lagier and Thomas, and obtained by exhausting the sulphuric charcoal with alcohol and distilling the solution to the consistence of an extract.

2. Garancin, first prepared by Lagier, Robiquet, and Colin, is obtained in a similar manner to sulphuric charcoal, excepting that a smaller quantity of acid is added (less than a third of the weight of the madder), and the mixture is more largely diluted with water and boiled for a longer time. The product is washed, dried, and ground with a small quantity of chalk or sodic carbonate to neutralise any acid that may be retained by the woody fibre. Madder yields from 33 to 36 per cent. of garancin. Garancin colours are regarded as somewhat less stable than those obtained directly from madder; but, if the garancin be well prepared, the colours are generally fine and brilliant, and the white ground remains intact. The violets which it produces are however not quite satisfactory, and to obtain a rose colour with it is very difficult.

3. Pincoffin, or *Alizarine commerciale*, introduced by Messrs. Pincoff and Co. of Manchester, is a garancin prepared and washed with the greatest care, then made as neutral as possible, and heated above 100° by high pressure steam, whereby a certain quantity of brown colouring matter is destroyed or rendered inert. This product yields very pure and bright violet tints without requiring clearing, and the other colours obtained with it are equally satisfactory.

4. Garanceux.—This is a product obtained by treating the waste madder of the dye-houses, which, as already observed, still retains a considerable quantity of colouring matter, with sulphuric acid, then filtering, washing, drying, and grinding. The substance thus obtained still dyes tolerably well, and may be used for a certain class of patterns not containing rose or violet tints.

5. Flowers of Madder (*Fleur de Garance*) is the name given to a kind of washed madder first prepared at Avignon by MM. Julien and Rocquer. The madder is suspended in water containing a small proportion of acid, partly to saturate earthy carbonates, partly to render the colouring principles less soluble. It is left in contact with the water for some hours, during which time alizarin and purpurin are formed, and become insoluble, and sometimes a true fermentation is set up. The product is then carefully washed, so as to remove only the more soluble matters. The first liquors, being strongly charged with sugar, are subjected to vinous fermentation, and on subsequently distilling them, a considerable quantity of alcohol is obtained. Madder yields about 50 per cent. of this product, which, being free from gummy and saccharine bodies, and especially from the brown colouring principle which soils the mordants, yield much finer colours than madder itself. More than half the quantity of madder cultivated at the present day is converted into flowers of madder and garancin.

6. Madder Extracts.—All the products above mentioned contain nearly the whole of the woody fibre of the root, an impurity which prevents their use in calico-

printing. To get rid of this, garancin or sulphuric charcoal, or flowers of madder, is treated with certain solvents, as in the preparation of colorin already mentioned, whereby the colouring matters are dissolved out and the woody fibre and other impurities are left behind. The solvents used for this purpose are:—

a. Aluminium-salts, alum being almost always the salt employed. The garancin, &c., is repeatedly boiled with an aqueous solution of alum, the colouring matter precipitated from the filtrate by sulphuric acid, and the precipitate collected and washed. The extract thus obtained almost always contains alumina, but is otherwise very pure, and yields very brilliant colours in dyeing and calico-printing; but the process is costly, because it requires large quantities of alum and sulphuric acid, and to recover the alum in the crystalline form, and separate it from the acid, the mother-liquors must be strongly concentrated in leaden vessels. Moreover, the residue of the madder, being impregnated with alum, which prevents its further use in dyeing, is totally lost.

b. Alkalis and Alkaline-salts.—The alkaline extracts are obtained by repeatedly treating madder or its derivatives with solution of caustic soda, carbonate or phosphate of sodium, or aqueous ammonia, filtering, precipitating the colouring matter by a mineral acid, filtering again, then washing and drying. This process is more economical than that with alum, but the extracts are much contaminated with resinous and pectous substances, very dark coloured, and when used for dyeing, yield colours which require very careful soaping and clearing, whereby the depth of the colour is greatly diminished. The extracts may however be improved in quality by boiling them, while yet moist, with dilute sulphuric acid, then filtering and washing.

c. Spirituous solvents.—The extracts prepared by treating good garancin or flowers of madder with alcohol or wood-spirit, have a fine yellow or yellow-brown colour, and dye very well, especially if they are preserved in the pasty condition. If they are thoroughly dried, the colouring matters become so completely enveloped by the resin, that they are very difficult to moisten, and nearly insoluble in water, even at the boiling heat.

d. Direct preparation of Rubian from Madder; E. Kopp's process (Bull. Soc. industr. de Mulhouse (1861) xxxi. 9; Rép. Chim. app. 1861, pp. 165, 223, 276; Jahresber. 1861, p. 938).—This process consists in the treatment of madder with *sulphurous acid*. It differs essentially from all the preceding both in principle and in practice, requiring the use, not of flowers of madder or garancin, but of madder in the natural state and as little altered as possible, in which, in fact, the colorific principle (rubian) has not yet been transformed into alizarin or purpurin, these compounds, when once formed, being no longer soluble in water containing sulphurous acid.

The process, as carried out on the large scale by MM. Schaaff and Lauth of Strasbourg, is as follows:—The ground madder is macerated for eight or ten hours with 10 or 12 times its weight of water containing 2 or 3 per cent. of sulphurous acid; the resulting solution is filtered, and the residue is pressed. On mixing the filtrate, which contains the colorific matter, with 3 per cent. of its weight of sulphuric acid, of specific gravity 1·52, and heating to 30° or 40° C., purpurin is deposited in large red or orange-coloured flakes, which are separated by decantation and filtration, and then washed.

The mother-liquor of the purpurin, heated to the boiling point, gives off carbonic acid, and yields a precipitate of alizarin coloured greenish-black by a foreign substance, which is likewise produced by the action of acids on the xanthin of MM. Kuhlmann and Higgin. This green alizarin is collected, filtered, and washed. It may be further purified by sublimation, or by solution in alcohol or wood-spirit.

The mother-liquor of the green alizarin contains the whole of the sulphuric acid used, together with the saccharine, gummy, and other matters extracted by the water from the madder. This acid liquor is used for converting into weak garancin, the madder-residue which has been exhausted by aqueous sulphurous acid and pressed. The mode of operating is exactly the same as for transforming fresh madder into garancin.

The mother-liquor of the garancin, which is still acid, but likewise saccharine, is neutralised with lime or chalk, and fermented so as to obtain alcohol.

This process is very simple and economical, the quantity of sulphuric acid consumed being about the same as employed in the preparation of ordinary garancin, and the only other material used being the small quantity of sulphur (or pyrites) required to produce the sulphurous acid.

By a careful experiment on the small scale, Kopp obtained from 100 pts. of Alsatian madder:

1·85	grms.	purpurin.	
3·15	„	green alizarin	dried at 40° C.
0·30	„	yellow „	
42·0	„	madder-residue dried at 40°.	
35·0	„	„ „	converted into garancin and dried at 100°;
82·30			

and he estimates the united colouring powers of these materials as equal to 1½ times that of the madder if employed in the crude state.

It does not appear likely that any other antiseptic substance can be advantageously substituted for the sulphurous acid. Kopp has unsuccessfully tried phenol, creosote, arsenious acid, and volatile oils; while the use of antiseptic salts, such as those of aluminium, mercury, copper, lead, &c. is inadmissible, because the residues, which always contain a portion of the colouring matter, would be contaminated with metallic oxides, and could not then be rendered available for dyeing, in the form of garancin or garanceux. (See Hofmann's *Report on Chemical Products and Processes in the International Exhibition of* 1862.)

7. Madder Lakes.—These lakes, which are obtained by precipitating aqueous extracts of madder or its derivatives with salts of aluminium, iron, tin, &c., but especially with aluminium-salts, possess a degree of fastness which withstands the strongest agents. They are, however, but little used in dyeing and calico-printing, on account of their high price, but are extensively employed as artists' pigments. For the preparation of an aluminous madder-lake, see LAKE (p. 466); also *Ure's Dictionary of Arts, &c.*, iii. 15.

The residue of madder treated with sulphurous acid by E. Kopp's process, but not yet exhausted, yields, when washed with boiling water, a yellow liquor still retaining a considerable quantity of colouring matter or of rubian. This liquor, mixed with a salt of aluminium more or less neutralised, furnishes, on boiling, fine red or rose-coloured lakes, according as the proportion of aluminium-salt is greater or smaller.

The same liquid mixed with milk of lime, produces, on boiling, a violet lime lake (a compound of alizarin and purpurin with lime), which may serve for producing, by double decomposition, other compounds of the colouring matter with metallic oxides; or, if decomposed with heated hydrochloric acid, it will yield the colouring matter in the form of a yellow or brownish-yellow extract resembling colorin (p. 748).

Valuation of Madder. The method usually adopted for ascertaining the value of any sample of madder, is to dye a certain quantity of mordanted calico with a weighed quantity of the sample, and compare the depth and solidity of the colours with those produced by the same weight of another sample of known quality.

Thibierge (Rép. Chim. app. 1863, p. 157) proposes to estimate the value of a sample of madder by precipitating the alcoholic tincture obtained by treating madder with 100 times its weight of alcohol, with a standard solution of neutral acetate of lead. A similar method was proposed some time ago by Basset, who, however, weighed the precipitate. Thibierge states that the colour of the precipitate obtained, especially if controlled by that of the precipitate produced by stannous chloride, is sufficiently characteristic to detect the presence of any adulteration. The method of precipitation with a standard solution of acetate of lead is certainly expeditious, but it remains to be proved that the precipitation is regular and complete, and that the result is not vitiated by the presence of any foreign body extracted from the madder by alcohol.

Madder is sometimes adulterated with sand, clay, brick-dust, ochre, saw-dust, bran, oak-bark, logwood, and other dye-woods, sumach, and quercitron-bark. Some of these adulterations are difficult to detect. Those which contain tannin may be discovered by the usual tests for that substance, since madder contains no tannin. If the adulteration is of a mineral nature, its presence may be detected by incinerating a weighed quantity of the sample. If the quantity of ash which is left exceeds 10 per cent., adulteration may be suspected.

MADDER, EAST INDIAN. See MUNJEET.

MADREPORES. Calcareous concretions produced by *polypi*, placed at the surface of calcareous ramifications which are fixed at their base, and perforated by numerous pores.

MAGISTERY. A term formerly applied to certain white precipitates; thus, the basic nitrate of bismuth thrown down on adding water to a solution of the metal in nitric acid, was called *magistery of bismuth*.

MAGMA. A precipitate or mass of crystals, or mixture of substances in a pulpy or pasty state.

MAGNESIA. The oxide of magnesium (p. 754).

MAGNESIA ALBA. A pharmaceutical preparation consisting of a mixture of several hydrocarbonates of magnesium obtained by precipitating a soluble magnesium-salt with an alkaline carbonate. (See CARBONATES, i. 788.)

MAGNESIA NIGRA. An old name for black oxide of manganese (*q. v.*)

MAGNESITE. Native carbonate of magnesium. (See CARBONATES, i. p. 787.)

MAGNESIUM. Syn. *Magnium.* Symbols and Atomic weights, Mg = 12 Mmg or ~~Mg~~ = 24.

This metal is usually classed with those whose oxides constitute the alkaline earths; but it is much more closely analogous to zinc than to any other element. It occurs in the mineral kingdom, as hydrate, carbonate, borate, phosphate, sulphate, chloride; and nitrate, sometimes in the solid state, sometimes dissolved in various mineral waters (including salt springs), and in sea-water; in a variety of minerals, consisting of silicate of magnesium combined with other silicates, as in soap-stone, meerschaum, steatite, ophite, tolite, anorthite, hornblende, asbestos, talc, augite, chrysolite,—and combined with aluminium, in spinel and zeilanite. It also occurs in the bodies of plants and animals, chiefly as carbonate and phosphate, and in combination with organic acids.

Our acquaintance with the compounds of this metal does not date from early times. The knowledge of carbonate of magnesium or *magnesia alba*, as a medicine, was first promulgated from Rome in the beginning of the eighteenth century. Valentin in 1707 and Slevogt in 1709, subsequently found the same earth in the mother-liquor of saltpetre and in Epsom salts. Hoffmann, Black, Margraf, and Bergman pointed out the characters which distinguish it from lime, with which it was at first confounded. Davy first obtained from it the metal magnesium, which Bussy succeeded in preparing in a state of greater purity. It has since been obtained in much larger quantities by Bunsen, Matthiessen, and Deville and Caron.

Preparation of the metal.—1. By heating the anhydrous chloride with potassium in a porcelain or platinum crucible. When cold, the contents of the vessel are digested in cold water, by which the soluble chlorides are dissolved out, and the metal is left as a grey powder, which can be melted into globules. (Bussy, Pogg. Ann. xviii. 140.)

2. *By the electrolysis of the fused chloride.* A porcelain crucible is divided in its upper part into two halves by a vertical diaphragm (made out of a thin porcelain crucible cover), and fitted with a cover (filled from a tile), through which the extremities of the carbon-poles of a galvanic battery are introduced into the two halves of the crucible. The crucible is then heated to redness, together with the cover and the poles, and filled with fused chloride of magnesium; and the salt is subjected to the action of a battery of 10 zinc carbon elements. The negative pole is cut like a saw (*fig.* 427, vol. ii. p. 438) so that the magnesium, as it separates, may lodge in the cavities, and not float on the surface of the specifically heavier liquid (Bunsen, Ann. Ch. Pharm. lxxxii. 137). According to Matthiessen (Chem. Soc. J. viii. 107), the metal may be much more easily obtained from a fused mixture of 4 at. chloride of magnesium and 3 at. chloride of potassium, which is prepared with greater facility than the pure anhydrous chloride of magnesium. The two salts mixed in the proper proportion * with a little chloride of ammonium, may be fused and electrolysed in Bunsen's apparatus just described, the cutting of the negative pole being, however, dispensed with, as the metal is heavier than the fused mixture. A very simple and convenient way of reducing the metal, especially for the lecture table, is to fuse the mixture in a common clay tobacco pipe over an argand spirit-lamp or gas-burner, the negative pole being an iron wire passed up the pipe-stem, and the positive pole a piece of gas-coke, just touching the surface of the fused chlorides. (Matthiessen.)

Magnesium may, however, be obtained in much larger quantity, by heating a mixture of 600 grms. of chloride of magnesium, 100 grms. fused chloride of sodium, and 100 grms. of pulverised fluoride of calcium, with 100 grms. of sodium, to bright redness, in a covered earthen crucible. The magnesium is thereby obtained in globules, which are afterwards heated nearly to whiteness in a boat of compact charcoal placed within an inclined tube of the same material, through which a stream of dry hydrogen is passed. The magnesium then volatilises and condenses in the upper part of the tube. Lastly, it is remelted with a flux composed of chloride of magnesium, chloride of sodium, and fluoride of calcium, and is thus obtained in large globules. It still, however, usually retains portions of carbon, silicium, and nitrogen, from which it may be purified by careful distillation in a current of hydrogen (Deville and Caron, Ann. Ch. Pharm. ci. 359). Sonstadt has recently prepared magnesium by this process on a considerable scale for commercial purposes.

Properties.—Magnesium on the recently fractured surface is sometimes slightly crystalline and coarsely laminated; sometimes fine-grained. In the former case, it is silver-white and shining; in the latter, bluish-grey and dull. Its specific gravity is 1·7430 at. + 5° C. (Bunsen); 1·75, according to Deville and Caron. It is about as hard as calcspar, and may be easily filed, bored, sawn, and flattened to a certain extent, but is scarcely more ductile than zinc at ordinary temperatures; it may, however, be drawn out into wire. It melts at a moderate red heat (Bunsen); melts and volatilises at about the same temperature as zinc (Deville and Caron). It does not alter in a dry atmosphere, but in damp air soon becomes covered with a film of hydrate of magnesium. Heated to redness in the *air*, or in *oxygen gas*, it burns with a dazzling bluish-white light, and forms magnesia. The light of burning magnesium is remarkably rich in chemical rays, and may be used for taking photographs. It decomposes pure cold *water* but slowly, *acidulated water* very quickly; when thrown on aqueous hydrochloric acid, it takes fire momentarily; strong *sulphuric acid* dissolves it but slowly; a mixture of *sulphuric acid* and *fuming nitric acid* does not act upon it at ordinary temperatures. It burns when heated in *chlorine gas;* also in *bromine-vapour*, though with less facility; in *sulphur* and *iodine-vapour* very brilliantly (Bunsen). It unites directly with *nitrogen*, forming a transparent crystallised nitride, Mg^3N. (Deville.)

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* The solution of the chloride of magnesium may be evaporated almost to dryness and analysed to find the proportion of anhydrous salt present.

Magnesium forms but one series of compounds, in which it is mono- or diatomic according to the atomic weight adopted, *e.g.*:

$$\begin{array}{rcccccc} \text{The chloride } MgCl & = & 12 & + & 35{\cdot}5 & = & 47{\cdot}5 \\ \text{or } Mmg''Cl^2 & = & 24 & + & 2\,.\,35{\cdot}5 & = & 95{\cdot}0 \\ \text{The oxide } Mg^2O & = & 2\,.\,12 & + & 16 & = & 40 \\ \text{or } Mmg''O & = & 24 & + & 16 & = & 40 \end{array}$$

MAGNESIUM, BROMIDE OF, $MgBr$ or $MmgBr^2$, is found in sea-water and in numerous salt springs. It is produced by heating magnesium in bromine-vapour, or by passing the vapour over an ignited mixture of magnesia and charcoal. In the anhydrous state, it is a white mass of crystalline aspect, which is not fusible below a red heat, and not volatile. It deliquesces rapidly in the air, and dissolves in water with a hissing noise and evolution of heat. The solution, which may also be produced by dissolving magnesia in hydrobromic acid, yields, by evaporation over oil of vitriol, crystals containing 3 at. water. When evaporated by heat, it gives off part of its hydrobromic acid, and leaves a mixture of magnesia and bromide of magnesium.

MAGNESIUM, CHLORIDE OF, $MgCl$ or $MmgCl^2$, is an ingredient of sea-water and of many salt-springs and other mineral waters. It is produced when magnesium burns in chlorine gas, also by passing a stream of chlorine over an ignited mixture of magnesia and charcoal. This, however, is not a good mode of preparation, because the chloride of magnesium has but little volatility, and does not separate easily from the charcoal. Neither can the anhydrous chloride be obtained by dissolving magnesia in hydrochloric acid and evaporating to dryness, because it is then partly decomposed by the water, giving off hydrochloric acid and leaving magnesia. The best mode of preparing it is to evaporate to dryness a solution of magnesia in hydrochloric acid mixed with sal-ammoniac, and ignite the residue in a platinum crucible. A double chloride of magnesium and ammonium is thus formed, from which the water is expelled before it can decompose the chloride of magnesium; and at a higher temperature the anhydrous double chloride is likewise decomposed, giving off sal-ammoniac, and leaving pure chloride of magnesium.

Anhydrous chloride of magnesium is a white translucent mass consisting of large, flexible crystalline plates, having a pearly lustre, and sharp bitter taste. It melts to a clear liquid at a low red heat. It dissolves readily in water, with considerable rise of temperature. The *hydrated chloride* is deposited from a hot concentrated solution on cooling, in needles and prisms containing $MgCl.3H^2O$. The crystals are highly deliquescent, dissolve in 0·6 pts. of cold water, in 0·273 pts. of hot water, and in 2 pts. of alcohol of specific gravity 0·817.

Chloride of magnesium unites with the alkaline chlorides. The *potassium-salt*, $KCl.2MgCl.6H^2O$, crystallises, by careful evaporation from the last mother-liquor of sea-water in rhombohedral crystals.—The *sodium-salt* contains, according to Poggiale (Compt. rend. xx. 1130), $NaCl.2MgCl.H^2O$.

MAGNESIUM, DETECTION AND ESTIMATION OF. Magnesium-salts are colourless, unless they contain a coloured acid. The carbonate, borate, phosphate, arsenate, arsenite, and many of the organic salts, are insoluble in water; but most of these salts are soluble in a solution of chloride of ammonium; most of the others are soluble. The aqueous solutions have a bitter taste. All magnesium-salts, excepting the ignited metaphosphate, dissolve in hydrochloric acid.

1. *Reactions in the dry way.*—All magnesium-salts containing volatile acids are decomposed by ignition, leaving a residue of magnesia. Magnesium-salts heated before the blowpipe with a small quantity of nitrate of cobalt, leave a rose-coloured residue.

2. *Reactions in Solution.*—Solutions of magnesium-salts are not precipitated by *sulphydric acid* or *sulphide of ammonium*. The *fixed alkalis* and their *carbonates* produce a white precipitate of hydrate or carbonate of magnesium, insoluble in excess of the reagent, but soluble in ammoniacal salts, especially of chloride of ammonium. If the solution contains ammoniacal salts, no precipitate is formed. *Ammonia* added to a neutral solution of magnesia, not containing any ammoniacal salt, throws down a

white precipitate, insoluble in excess of ammonia; but if the solution previously contained an excess of acid, no precipitate is formed, the magnesium being kept in solution by the ammoniacal salt produced, and even when the original solution is neutral, only a part of the magnesia is precipitated, the rest being held in solution in the same manner. Magnesium-salts are not precipitated by *carbonate of ammonium*, *ferrocyanide of potassium*, or *alkaline sulphates*. *Baryta* or *lime-water* added to the solution of a magnesium-salt forms a precipitate of hydrate of magnesium. This reaction affords an easy method of separating magnesia from the alkalis.

Ordinary phosphate of sodium added to a neutral solution of a magnesium-salt produces a gelatinous precipitate of phosphate of magnesium, soluble in nitric or hydrochloric acid; but if ammonia be then added in excess to the acid solution, a precipitate of phosphate of magnesium and ammonium ($Mg^2NH^4PO^4$) is formed, which is flocculent or gelatinous at first, but soon becomes crystalline, especially on agitation. The same precipitate is likewise produced on adding a soluble phosphate to the solution of a magnesium-salt already containing ammonia. It is an extremely delicate test of the presence of magnesia. If the solution is very dilute, the precipitate attaches itself in crystalline grains to the sides of the vessel. According to Harting (J. pr. Chem. xxii. 50), a solution containing only $\frac{1}{900,000}$ of magnesia, gives a precipitate, after 24 hours with phosphate of ammonium mixed with free ammonia, provided the latter solution is highly concentrated and added in equal quantity. *Oxalic acid* or *acid oxalate of potassium* precipitates neutral magnesium-solutions, provided no ammoniacal salts are present.

3. *Quantitative Estimation and Separation.*—When magnesia occurs in a solution not containing any other fixed substance, its quantity may be determined by evaporating to dryness, igniting the residue, then moistening it with sulphuric acid slightly diluted with water, and expelling the excess of that acid at a low red heat: sulphate of magnesium then remains, containing 33·7 per cent. of magnesia, or 19·22 per cent. of magnesium.

If the solution contains other fixed substances, the magnesia must be precipitated by the addition of *ammonia* in excess and *phosphate of sodium*. The precipitated ammonio-magnesian phosphate does not settle down at once, but its deposition may be accelerated by leaving the vessel in a warm place. Care must be taken, however, not to allow the liquid to get very hot, as in that case, hydrate of magnesium will be precipitated, and will be very difficult to redissolve. The precipitate, after standing for about two hours, is collected on a filter and washed with water containing ammonia, as pure water decomposes it. It is then dried and ignited, whereby it is converted into pyrophosphate of magnesium, $2Mg^2O.P^2O^5$ or $Mg^4P^2O^7$, containing 36·33 per cent. magnesia, or 21·62 per cent. magnesium.

From the heavy metals, magnesium may be separated, either by *sulphydric acid* or by *sulphide of ammonium;* from aluminium and the other metals of the earths proper, also by sulphide of ammonium. In precipitating by sulphide of ammonium, however, it is necessary to guard against the simultaneous precipitation of small quantities of magnesia, for which purpose the ammoniacal liquid should be boiled, before filtering, till the excess of ammonia is expelled; any magnesia that may have been precipitated will then be redissolved (H. Rose, Pogg. Ann. cx. 411). For the separation of magnesium from manganese, see MANGANESE.

From aluminium, magnesium may be separated by precipitating the former with *hyposulphite of sodium* (i. 155).

From barium and strontium, magnesium is separated by *sulphuric acid;* from calcium by *oxalate of ammonium*, with addition of chloride of ammonium, to prevent the precipitation of the magnesia. When, however, the quantity of calcium present is very small in proportion to the magnesium, this mode of precipitation does not give exact results; and it is better, according to Scheerer (Ann. Ch. Pharm. cx. 36), to convert the two metals into sulphates; dissolve the sulphates in water; carefully add alcohol with stirring, till permanent turbidity is produced; leave the liquid to itself for a few hours, by which time the sulphate of calcium will be completely precipitated, together with a small quantity of sulphate of magnesium; wash the precipitate on a filter with alcohol diluted with an equal volume of water; then redissolve t in water, add hydrochloric acid in excess, and precipitate the lime with oxalic acid and ammonia.

From the alkali-metals, magnesium may be separated by converting the bases into sulphates, and adding *baryta-water*. The magnesia is then precipitated in the form of hydrate, together with sulphate of barium. The precipitate, after washing, is digested with dilute sulphuric acid, which extracts the magnesia in the form of sulphate; and the filtrate, containing the alkalis together with the excess of baryta, is also treated with sulphuric acid, which precipitates the baryta, and converts the alkalis into sulphates.

Magnesium may also be separated from the alkali-metals by means of *mercuricoxide*, The solution, from which all metals except those of the alkalis and magnesium have been removed, and which must contain no fixed acid, is digested with excess of finely divided mercuric oxide; the whole evaporated to dryness, and the residue heated to drive off the mercury. The magnesium then remains as magnesia, and the alkalis can be washed out with water.

Chancel (Compt. rend. 194), recommends the following method. The magnesia is precipitated from the solution containing sal-ammoniac and free ammonia, by *phosphate of ammonium;* the filtrate is evaporated to dryness; the residue carefully ignited to expel ammoniacal salts; then redissolved in water; and the solution is mixed with nitrate of silver and a slight excess of carbonate of silver. After filtering off the phosphate of silver (and chloride, if the alkalis existed in the solution as chlorides), the excess of silver is removed from the filtrate by hydrochloric acid, and the alkalis are estimated as chlorides.

4. *Atomic Weight of Magnesium.*—Berzelius found that 100 pts. of magnesia, dissolved in pure sulphuric acid and ignited, gave 293·85 of sulphate of magnesium, Mg^2SO^4, whence the atomic weight of magnesium would be 12·62, a result too high according to later experiments.

Scheerer (Pogg. Ann. lxix. 135), by determining the quantity of sulphate of barium produced from a given quantity of sulphate of magnesium, found for magnesium the number 12·1. The results of Svanberg and Nordenfeldt (J. pr. Chem. xlv. 473), obtained by the decomposition of oxalate of magnesium ($Mg^2C^2O^4.2H^2O$), made it 12·35; those obtained by converting a known weight of magnesia into sulphate gave it as 12·37; whilst those of Marchand and Scheerer (Ann. Ch. Pharm. lxxvi. 219), obtained by igniting the native carbonate (magnesite) gave the number 12·02. Dumas (Ann. Ch. Phys. [3] lv. 129) attempted to determine the atomic weight of magnesium by precipitating the chloride with nitrate of silver, but he found the greatest difficulty in obtaining the chloride free from magnesia. The mean of eleven experiments gave Mg = 12·3.

The mean of all these results is 12·16, but those of Marchand and Scheerer are generally regarded as the most trustworthy. Moreover Scheerer has lately shown, by his method of separating calcium and magnesium above given (p. 753), that the specimens of magnesite used by himself and Marchand in their determinations, contained small quantities of calcium not previously detected. He therefore considers that the number 12·02 found in those experiments was rather above than below the truth. On the whole, then, the atomic weight of magnesium may be regarded as 12 for Mg (monatomic), or 24 for Mmg (diatomic).

MAGNESIUM, FLUORIDE OF. Obtained as a white tasteless powder by treating the carbonate with hydrofluoric acid, or mixing the sulphate with fluoride of potassium. It is insoluble in water and nearly insoluble in acids.

MAGNESIUM, FLUOBORIDE OF. See BOROFLUORIDES (i. 634).

MAGNESIUM, FLUOSILICIDE OF. See SILICOFLUORIDES.

MAGNESIUM, IODIDE OF. Obtained by evaporation of its solution, as a difficultly crystallisable hydrate, which deliquesces in the air, and when heated gives off hydriodic acid and leaves pure magnesia.

MAGNESIUM, NITRIDE OF. Mg^3N or Mmg^3N^2.—Deville and Caron (Compt. rend. xliv. 394), by distilling impure magnesium, obtained a black residue, and a distillate of magnesium covered with small transparent needles, which easily decomposed, with formation of magnesia and ammonia, and therefore contained a nitride of magnesium. Briegleb and Geuther (Ann. Ch. Pharm. cxxiii. 228) have obtained the same compound, in the amorphous state, by igniting metallic magnesium in ammonia or in nitrogen gas; the latter method giving the purest product. Nitride of magnesium thus prepared is a greenish-yellow amorphous mass, becoming brownish-yellow when hot. Heated in dry oxygen gas, it oxidises to magnesia, with vivid incandescence. It is decomposed by air and water, the reaction in the latter case being violent enough to make the water boil. Acids both dilute and concentrated, with the exception of strong sulphuric acid, form ammonium- and magnesium-salts, even in the cold; strong sulphuric acid, only when heated, and with evolution of sulphurous anhydride. The nitride heated in hydrochloric acid gas, yields chloride of ammonium and chloride of magnesium; in sulphydric acid, the corresponding sulphides. Carbonic anhydride and dry carbonic oxide decompose it, at the heat of a strong air-furnace, with separation of carbon and formation of cyanogen. When vapour of penta-chloride of phosphorus is passed over nitride of magnesium heated in a stream of nitrogen, the nitride is converted into a greyish-white substance, probably P^3N^5, according to the equation:

$$3PCl^5 + 5Mg^3N = 15MgCl + P^3N^5$$

When nitride of magnesium is heated to 160°—180° in a sealed tube with oxychloride of phosphorus, and the excess of oxychloride is distilled off, there remains a residue which melts at 220°, and dissolves completely in water, with great evolution of heat, forming a solution which gives, with acetate of barium, a precipitate of metaphosphate of barium. Absolute alcohol and iodide of ethyl do not act on nitride of magnesium, even at 160°.

MAGNESIUM, OXIDE OF. *Magnesia.* Mg^2O or $MmgO$.—This earth, which is the only known oxide of magnesium, is produced in the form of a white amorphous powder, when magnesium burns in the air or in oxygen-gas, and remains in the same state when the carbonate, nitrate, or any other salt of magnesium containing a volatile acid, is ignited in the air. It may be obtained crystallised in cubes and regular octahedrons, by strongly igniting amorphous magnesia in a stream of hydrochloric acid-gas (H. Deville, Ann. Ch. Pharm. cxx. 280; Jahresb. 1861, p. 7); also, according to Debray and Kuhlmann (Ann. Ch. Pharm. cxx. 283), by strongly igniting a mixture of sulphate of magnesium and an alkaline sulphate in a platinum crucible, so that the magnesia separated by the heat may crystallise from the fused alkaline sulphate. A mixture of magnesia and ferric oxide, strongly ignited in hydrochloric acid gas, yields a mixture of shining black octahedrons of magno-ferrite, $MmgO.Ffe^2O^3$ or $\left.\begin{matrix}Mmg'' \\ \overset{'''}{F}fe^2\end{matrix}\right\}O^4$, and slightly coloured regular octahedrons of magnesia containing a small quantity of iron, exactly resembling periclase, a mineral consisting of magnesia with 1 part in 25 of ferrous oxide, which occurs disseminated through ejected masses of white limestone, and in spots of clustered crystals, on Monte Somma.

Ordinary calcined magnesia is prepared by gentle but prolonged ignition of the carbonate. It is a fine, white, very bulky powder, of specific gravity 3·07 to 3·200, increased by ignition in a pottery-furnace to 3·61 (H. Rose). It melts only at the very highest temperatures, as in the oxyhydrogen blowpipe flame, to which it imparts a pale red colour, and is then converted into a sort of enamel, which scratches glass like a diamond (Clarke). It is tasteless and inodorous; changes some of the more delicate vegetable colours, as that of moistened red litmus paper, like the alkalis; it is not caustic. It is partially decomposed by potassium at a white heat. It is very slightly soluble in water; in 55,368 pts., either cold or boiling, according to Fresenius (Ann. Ch. Pharm. lix. 117), the solution having a faint alkaline reaction.

A *hydrate of magnesium*, $MgHO$ or $MmgH^2O^2$, occurs native in rhombohedral forms, as brucite (i. 684), and is precipitated as a white powder on adding potash, soda, or baryta-water in excess to the solution of a magnesium-salt.

MAGNESIUM, SULPHIDE OF. A sulphide of magnesium is obtained, mixed, however, with magnesia, by heating a mixture of charcoal and sulphate of magnesium. A purer product is obtained by adding to the preceding mixture, an alkaline persulphide, or a mixture of carbonate of sodium with excess of sulphur. According to Frémy, sulphide of magnesium is easily produced by passing the vapour of sulphide of carbon over red-hot magnesia.

Solutions of magnesia are not precipitated by alkaline sulphides, but on mixing sulphate of magnesium with sulphide of barium, sulphate of barium is precipitated, and sulphide of magnesium remains in solution. Sulphide of magnesium is likewise obtained by passing sulphydric acid gas in excess into water containing magnesia in suspension. A solution of sulphide of hydrogen and magnesium is then formed, which is decomposed by boiling, into sulphydric acid, and a white gelatinous mass of sulphide of magnesium.

Sulphide of magnesium forms double salts with sulphide of carbon, and with the sulphides of arsenic.

Sulphide of magnesium is decomposed, by the continued action of water, into magnesia and sulphydric acid. The presence of that acid in mineral waters may, perhaps, be accounted for by the existence of sulphide of magnesium in the strata through which those waters percolate. (Pelouze and Frémy, *Traité*, ii. 286.)

MAGNESIUM-ETHYL. MgC^2H^5 or $Mmg(C^2H^5)^2$.—When iodide of ethyl is added to magnesium-filings contained in a strong narrow glass tube, an action immediately takes place, attended with rise of temperature, and evolution of a considerable quantity of gas containing ethylene, and apparently also ethyl and hydride of ethyl. If the tube, after being cooled with cold water, be sealed and heated for some hours to 120°—130°, the contents solidify to a white mass, which, when subsequently distilled, yields a residue of iodide of magnesium, and a distillate containing undecomposed iodide of ethyl, and magnesium-ethyl, which may be separated by fractional rectification.

Magnesium-ethyl is a colourless liquid, having a strong alliaceous odour, and boiling at a higher temperature than iodide of ethyl. It takes fire in the air, and decomposes water with violence. (Cahours, Ann. Ch. Pharm. cxiv. 227, 354; Jahresb. 1859,

p. 416. See also Hallwachs and Schafarik, Ann. Ch. Pharm. cix. 215; Jahresb. 1859, p. 407.)

Magnesium-ethyl forms a finely-crystallised double salt with iodide of magnesium: probable formula, $MmgC^2H^5I$. (Wanklyn.)

MAGNESIUM-METHYL is produced by the action of magnesium on iodide of methyl in a manner similar to the above. It is likewise a mobile strong-smelling liquid, which instantly takes fire in the air, and quickly decomposes water, with evolution of marsh gas and separation of magnesia. (Cahours.)

MAGNETIC IRON ORE. Native ferroso-ferric oxide (iii. 337, 397).

MAGNETIC PYRITES. Ferroso-ferric sulphide (iii. 401).

MAGNETISM. It has been known from very early times, that the native black oxide of iron, or ferroso-ferric oxide (Fe^3O^4) possesses, at certain points of its surface, called poles, the power of attracting small pieces of iron. The Greeks gave to this mineral the name of *magnetes* (*μάγνητης*), from the village of Magnesia in Lydia, near which it was found in considerable quantity: hence the name Magnetism, applied to the branch of science which treats of this peculiar kind of attraction, and of the various phenomena related to it.

The attractive power of the natural magnet may be communicated to iron and steel by contact, the attractive power thus developed continuing, in soft iron, only so long as the contact lasts, whereas, in hard iron, and more especially in steel, it continues after separation from the natural magnet. A bar of steel rubbed lengthwise, and in one constant direction, with the pole of a natural magnet, becomes itself a magnet, capable of attracting iron, and imparting its power in like manner to other bars of steel.

Another mode of imparting magnetism to iron or steel is by the action of an electric current or discharge, as already described in the article Electricity (ii. 448). A steel bar, placed within a helix of wire through which an electric current is passed, becomes a permanent magnet. Lastly, as we shall presently explain more particularly, a bar of iron or steel may be rendered magnetic by placing it in a certain position relatively to the earth.

The properties of magnets are the same in whatever manner their power may be developed.

There are only two other metals, viz. nickel and cobalt, in which the magnetic power can be conspicuously developed by the means above mentioned: in nickel it is considerable, but much less powerful than in iron; and in cobalt, still less. All other bodies are, indeed, more or less susceptible of magnetic influence, but they exhibit its effects only when subjected to very powerful electric or magnetic forces; and, in many cases, the mode of manifestation is very different from that which is exhibited by iron. See Diamagnetism (p. 770).

Distribution of Magnetic Power.—In a magnetised steel bar, as in the natural magnet, the attractive power is not uniformly distributed, but is more or less concentrated in certain points called poles, situated at or near the ends of the bar, whence it diminishes with greater or less rapidity and regularity towards an intermediate point, or rather line, called the median line, generally in the middle of the bar. This may be shown by rolling the bar in iron filings, which then attach themselves in clusters round the ends, leaving the middle bare, as in *fig.* 716. If the two poles have equal attractive power, and are situated at equal distances from the ends, and the power diminishes from each of them at the same rate towards the middle, the bar is said to be *regularly*

Figs. 716.

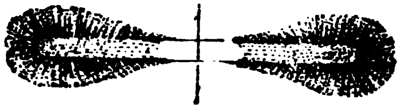


Fig. 717.

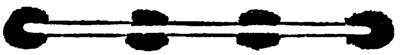
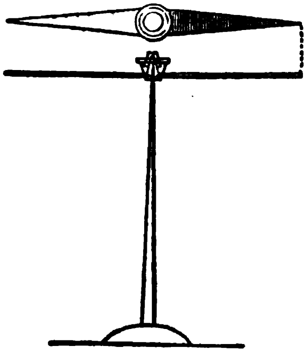


Fig. 718.



magnetised. This, however, is not always the case. Sometimes a magnet exhibits more than two poles, as shown in *fig.* 717.

Direction of a freely-suspended Magnetic Bar.—When a regularly magnetised steel bar is suspended by its centre of gravity from a thread without torsion, or supported by an agate cap on a steel point, as in *fig.* 718, so that it can move freely in a horizontal plane, it takes up a particular position with respect to the poles of the earth, one end pointing more or less exactly towards the north, the other to the south. A bar-magnet thus suspended is called a magnetic needle, though the so-called needle is sometimes a stout bar weighing several pounds. Small needles are sometimes made of flat lozenge-shaped bars of steel, like that represented in *fig.* 718.

The particular angle which the bar in its position of equilibrium makes with the geographical meridian is different on different parts of the earth's surface, and varies at the same place at different times. In some parts, the suspended magnet points exactly north and south; in London, at the present time (1864), the direction is north-west and south-east, the position of equilibrium making an angle of 20° 45′ with the geographical meridian.

The vertical plane passing through the two poles of the needle is called the magnetic meridian of the place, and the angle which it makes with the geographical meridian is called the declination.

One particular end of the suspended bar always points towards the north, the other towards the south. If the bar be placed exactly in the opposite position, it may remain for a while in a condition of unstable equilibrium; but the slightest disturbance will cause it to swing back to its former position, in which, after a certain number of oscillations, it will come to rest. The two ends of the bar are accordingly designated as the north and south poles respectively.* Every regularly magnetised piece of iron or steel has two such poles, and two only, which are not interchangeable.

If the magnetic needle, instead of having its movements restricted to a horizontal plane, be suspended by its centre of gravity, in such a manner that it can move freely in all directions, it places itself, not only in the magnetic meridian, but likewise at a particular inclination to the horizon, which also differs according to the locality, and varies in the same place at different times. In London, at the present time, a freely suspended magnetic needle places itself at an angle of 68° 15′ to the horizon, with its north pole downwards. A magnet, suspended so as to exhibit this inclination, is called a dipping needle, and the angle of inclination is called the dip.

The north pole of the needle dips throughout the greater part of the northern hemisphere, and the south pole throughout the greater part of the opposite hemisphere, and between these two portions there is a line not deviating greatly from the earth's equator, on which the needle has no dip, but stands horizontally. In short, as will be seen from what follows, the movements of a freely-suspended needle in different parts of the world, are such as may be accounted for by regarding the earth as a great magnet, the northern hemisphere exhibiting southern, and the southern hemisphere northern magnetic polarity. (See MAGNETISM, TERRESTRIAL.)

MAGNETIC ATTRACTION AND REPULSION.

A piece of unmagnetised iron is attracted indifferently by either pole of a magnet, and, it need scarcely be observed, that the attraction is mutual, so that, whichever of the two is movable, will move towards the other; and if both are movable, they will approach one another with velocities which are inversely as their masses. Hence, if a piece of unmagnetised iron or steel be presented to either pole of a magnetic needle, the needle will move towards it. But, when a magnetised bar is presented to the needle, it is found that the north pole of the one attracts the south pole of the other, but repels the north, while a south pole attracts a north pole, but repels a south. The general law of magnetic attraction and repulsion is then exactly similar to that of electric attraction and repulsion (ii. 376), viz. *Similar magnetic poles repel, dissimilar poles attract one another.* Hence, to determine whether any piece of iron or steel is magnetised or not, it is sufficient to present the several parts of its surface to a delicately-suspended magnetic needle: if every part attracts the needle, the piece of iron is destitute of magnetic polarity; if, on the other hand, some parts attract, while others repel, the poles of the needle, the iron is shown to be magnetic, and the number and positions of its poles may be determined.

Magnetic attraction and repulsion are not prevented by the interposition of any substance not itself susceptible of magnetism. If a magnetic needle be deflected from its natural position, by placing a piece of iron, or another magnet, near it, and allowed to settle itself in its position of equilibrium, that position will not be disturbed by the interposition of a screen of paper, wood, glass, copper, &c.; but, if a plate of iron be interposed, the needle will immediately take up a new position, the distribution of the magnetic forces being altered by the interposition of the iron.

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* Sometimes by English writers, and commonly by French authors, the pole which points northwards is called the south pole (*pôle austral*), and that which points southwards the north pole (*pôle boréal*) of the magnet. In order to avoid this confusion, Faraday speaks of the pole which points northwards as the "marked pole."

The force of magnetic attraction and repulsion varies inversely as the square of the distance between the poles or centres of action.—By the term *pole* we must here understand the point of application of all the forces exerted by one half of a magnet on any point of the other. It is evident, then, that the poles must vary in position according to the distance between the magnets; but unless the magnets are very close together, the distance between their poles will not differ sensibly from that which exists when the magnets are placed so far apart that all the acting forces may be regarded as parallel. The poles, understood in this sense, do not of course coincide with the points of strongest attraction, which are generally at the ends of the magnet, but they are nearer to those points in proportion as the magnetic power decreases more rapidly from the ends towards the middle.

This law of magnetic action may be demonstrated in three ways: 1. *By the Torsion-Balance.*—The construction of the magnetic torsion-balance is similar to that already described (ii. 380) for the measurement of the electric forces, the shellac needle being replaced by a magnetic needle, and the shellac stem by a bar-magnet. The mode of experimenting to determine the law of magnetic action with regard to distance, is exactly similar to that described at page 381, vol. ii., for measuring the force of electric attraction and repulsion.

2. *By the Method of Oscillations.*—Suppose a magnetic needle to be placed near a bar-magnet, with its centre on the prolongation of the axis of that magnet; it will then place itself in the direction of that axis, and if disturbed from that position will oscillate backwards and forwards, and ultimately settle in its original position of equilibrium. Now the oscillations of the needle thus vibrating under the influence of magnetic attraction, are regulated by the same laws as those of a pendulum oscillating under the influence of gravity, that is to say, *the squares of the times of oscillation are inversely as the attracting forces.* Supposing then the power of the magnet and needle to remain constant during the experiment, the diminution of the attractive force at different distances may be measured by counting the number of oscillations which the needle performs in a given time at different distances. It is necessary to observe, however, that, as the oscillations of the needle are determined by the magnetic force of the earth as well as by that of the magnet, the terrestrial force must be either compensated or allowed for.

To simplify the calculations as much as possible, the experiment may be performed with an *astatic needle*, that is to say, a system composed of two magnetic needles of equal power, joined together parallel to one another, but with their poles in contrary directions, by a small piece of straw or copper wire passing through their centres of gravity (ii. 443); such a combination will evidently place itself indifferently in all positions relatively to the magnetic meridian, because the magnetic force of the earth acts on the two needles composing it with equal force but in opposite directions. Now let one of the poles of such a needle be brought near the contrary pole of a bar-magnet, of such a length that the action of its farther pole may be left out of account. The distance between the poles of the magnet and needle is then to be measured, the needle made to vibrate, and the number of its oscillations performed in a given time, counted. The needle is then removed to a greater distance and the experiment is repeated. If then m and m' are the magnetic forces at the distances d, d', and n, n' the corresponding numbers of oscillations in the same time; we have $n^2 : n'^2 = m : m'$. Now experiment shows that the quantities $n, n'\ d, d'$ are related by the equation $n : n' = d' : d$, that is to say, the number of oscillations in a given time are inversely as the distances; consequently

$$m : m' = d'^2 : d^2.$$

The same result may be attained by the use of a needle not rendered astatic. Let N be the number of oscillations which it makes in a given time under the influence of the earth's magnetism alone; n the number performed in the same time under the joint influence of the terrestrial force and that of a magnet placed at a certain distance from the needle in the magnetic meridian; and n' the number performed in like manner when the magnet is removed to a greater distance. If then the magnetic forces of the earth, and of the magnet at the two distances mentioned, be denoted by F, m, m' respectively, we shall have

$$N^2 : n^2 = F : m + F$$

$$\text{and } N^2 : n'^2 = F : m' + F$$

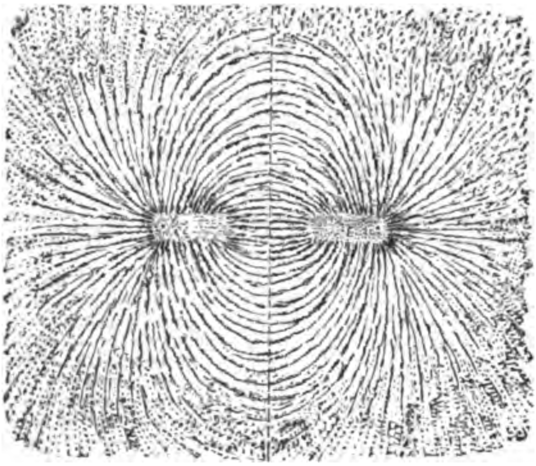
$$\text{therefore } n^2 - N^2 : N^2 = m : F$$

$$\text{and } n'^2 - N^2 : N^2 = m' : F$$

$$\text{and finally } m : m' = n^2 - N^2 : n'^2 - N^2.$$

3. *By the Form of the Magnetic Curves.*—Place a bar-magnet under a sheet of stiff paper, and sprinkle some fine iron filings on the paper through a gauze sieve. These filings will arrange themselves round the magnet in peculiar curves (*fig.* 719), radiating as it were, from the two poles. Now these curves are clearly the graphic expression of the law of magnetic attraction and repulsion with regard to distance: for each of the filings under the influence of the magnet becomes itself a small magnet, the poles of which place themselves in a position determined by the resultant of the forces exerted upon them by the two poles of the magnet; and this position of equilibrium varies according to the distance of the filing from the two poles respectively. In fact, a small magnetic needle, placed on any part of the paper, will settle itself in the direction of a tangent to the curve passing through that point. If placed on any point of the prolongation of the axis of the magnet, it will take up a position parallel to that axis with its poles arranged consecutively with those of the bar-magnet; at any point on the line drawn through the centre of the magnet at right angles to its axis—every point of which line is equidistant from the two poles—the needle will place itself parallel to the bar-magnet, with its poles in the contrary direction; and in any intermediate position, the needle will place itself obliquely to the magnet, its inclination increasing with the difference of its distances from the two poles.

Fig. 719.



If then the mode of generation of the magnetic curves—or, what comes to the same thing, their general equation—can be determined, the law of force with regard to distance may be deduced from it. The curves may be obtained in a state convenient for measurement by forming them over a plate of glass in the manner above described, and laying upon it a sheet of paper covered with gum or starch paste. In this manner the filings will be fixed on the paper, and the curves may be measured.

By careful measurements of the curves formed by the joint action of two magnetic poles, either contrary or similar, on iron filings or infinitely small magnets, Roget has determined the following law: *The difference of the cosines of the angles formed with the magnetic axis (the line joining the two poles) by lines drawn from these two poles to any point of a magnetic curve, is a constant quantity, the two angles being taken on the same side of the axis.*

Roget has described an instrument for tracing the curves by continued motion, founded on this property, and has also given the following method for describing them by points.

From each pole as a centre, and with any radii whatever, describe two circles; produce the axis till it meets both these circles; divide the whole length into any number of equal parts, and project each point of division perpendicularly on the two circumferences. If radii indefinitely prolonged be then drawn through the centre of each circumference and the points thus determined upon it, these radii will intersect one another in points belonging to the curves.

If the two acting poles are of contrary name, the curves are said to be *converging* (*fig.* 719), and are the curvilinear diagonals in the direction of the magnetic axis of the quadrilaterals formed by the intersection of the rays. If on the other hand the two poles are of the same name, the curves are said to be *divergent*, their direction being that of the curvilinear diagonals perpendicular to the former.

Now let A, B (*fig.* 720) be the two magnetic poles, M a point of the curve whose co-ordinates, referred to two rectangular axes, are x and y. Let AB be the axis of x, and its middle point, O, the origin. Also let $OA = OB = h$; $AM = r$; $BM = r'$; angle $MAB = i$; $MBA = i$. Then $AP = h - x = r \cos i$; therefore $\cos i = \frac{h-x}{r}$; in like manner $\cos i' = \frac{h+x}{r}$. Therefore, according to Roget's law,

$$\frac{h-x}{r} \pm \frac{h+x}{r'} = \text{constant};$$

$$\text{or} \quad \frac{h-x}{\sqrt{(h-x)^2+y^2}} \pm \frac{h+x}{\sqrt{(h+x)^2+y^2}} = \text{constant}.$$

This is the equation of the magnetic curves, the upper or lower sign being taken according as the two poles are opposite or similar.

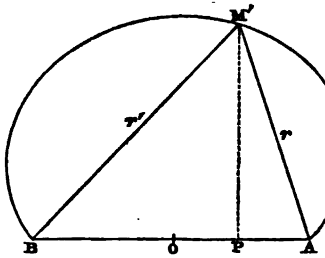


Fig. 720.

From this equation, by the processes of the differential calculus, the expression of the inclination of the tangent to the curve at any point may be found; and as this tangent is the direction assumed by a magnetic needle having its centre placed over the point of contact with the curve, which direction is determined by the resultant of the attractive and repulsive actions exerted upon it by the two poles A, B, it follows that the value of this inclination, properly expressed in terms of the distance of the point of contact from the two poles, will give the law of variation of the intensity according to the distance. When these calculations are made, it is found, in accordance with the results of the other modes of measurement above described, that the intensity of the force of magnetic attraction and repulsion varies inversely as the square of the distance. (See De La Rive, *Traité de l'Electricité*, tome i. note D, p. 592.)

Comparison of the Power of different Magnets. Distribution of Magnetism.

The old method of comparing the power of magnets, or of different parts of the same magnet, consisted in ascertaining the weights which they were capable of supporting. This method, however, can give only a rough approximation to the truth, inasmuch as the weight which a magnet can support depends in great measure on the manner in which the weight is applied, and on the rate at which it is increased. When the weight with which a magnet is loaded is very gradually increased, it is found to be capable of supporting a much larger weight than could be supported by it if applied all at once.

Much more exact results are obtained with the torsion balance and by the method of oscillations, both of which methods have been applied to this purpose by Coulomb.

To compare the force of two or more magnets by the torsion balance, these magnets are introduced successively through the hole m (*fig.* 373; ii. 380) and the needle of the balance is kept at a constant angular distance by twisting the thread through different angles, which are to one another as the forces to be overcome. When the method of oscillations is employed, the magnets are placed successively at a constant distance from the needle, this distance being so great that they cannot alter the distribution of its magnetic power.

Magnetic Moments.—Another mode of comparing the power of magnets is to place each of them successively in a small stirrup suspended from the thread of the torsion-balance, so that the magnet may remain in the magnetic meridian when the thread is untwisted. The thread has then to be twisted through different degrees, so as to obtain for each magnet the same angle of deviation from the magnetic meridian. The angles of torsion thus found represent what Coulomb calls the magnetic moments of the several bars. It is evident that the magnetic moment depends both on the magnetic intensity of the bar, and on the distance of its poles from the axis of suspension.

Distribution of Magnetism.—To measure the relative attractive or repulsive forces exerted by the different parts of a bar-magnet, Coulomb introduced a vertical wooden rule into the glass case of the torsion-balance, in such a position that it touched the needle of the balance which rested in the magnetic meridian when the thread was untwisted. At the back of this rule was a vertical groove in which the magnet to be tested was made to slide up and down, so as to bring the several parts of its length opposite to the pole of the needle of the same name as the half of the bar which was presented to it. The needle was thereby repelled; and to bring it back to its original position, the thread had to be twisted through a certain angle, which measured the repulsive force exerted. The bar was then shifted in the groove, so as to bring another part of it opposite to the pole of the needle, and a similar experiment was made. The magnetic bar being very close to the needle, it is only the points very nearly on a level with the needle that can exert any sensible influence over it, those which are even a few millimetres above or below, acting too obliquely.

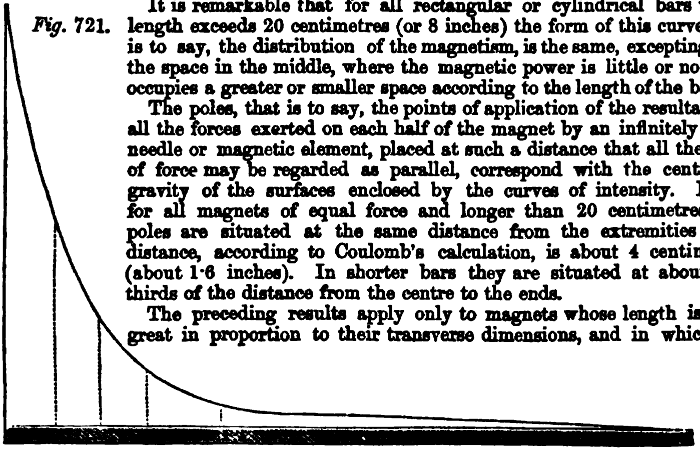
In applying the method of oscillations to the same purpose, a small needle, magnetised to saturation, so that its magnetic state may not be altered by the action of the bar, is made to oscillate near different parts of the bar. Denoting by m, m' the magnetic intensities at two different points, and by N, n, n' the number of oscillations made in a given time, under the influence of the earth alone, and under this influence added to that of the two points of the bar under consideration, we find, as on page 758,

$$m : m' = n^2 - N^2 : n'^2 - N^2.$$

Either of these methods gives directly the relative magnetic intensity of any part of a bar, excepting at the extremities, for which the intensities found by direct experiment must be doubled, in order to give the true force at these points, as compared with the rest: for the power observed at these extreme points would evidently be double of what it actually appears to be, if the magnet were prolonged, so as to present, beyond these extremities, points of equal magnetic force with those which are within them, as is the case for every other part of the bar.

The results obtained by these methods may be represented graphically by erecting, at the several points of a horizontal line representing a magnetised bar, perpendiculars whose lengths are proportional to the intensities observed at these points. The ends of these ordinates form a curve like that represented in *fig.* 721.

Fig. 721.



It is remarkable that for all rectangular or cylindrical bars whose length exceeds 20 centimetres (or 8 inches) the form of this curve, that is to say, the distribution of the magnetism, is the same, excepting that the space in the middle, where the magnetic power is little or nothing, occupies a greater or smaller space according to the length of the bar.

The poles, that is to say, the points of application of the resultants of all the forces exerted on each half of the magnet by an infinitely small needle or magnetic element, placed at such a distance that all the lines of force may be regarded as parallel, correspond with the centres of gravity of the surfaces enclosed by the curves of intensity. Hence for all magnets of equal force and longer than 20 centimetres, the poles are situated at the same distance from the extremities: this distance, according to Coulomb's calculation, is about 4 centimetres (about 1·6 inches). In shorter bars they are situated at about two thirds of the distance from the centre to the ends.

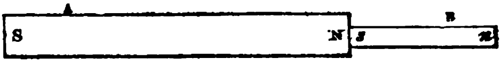
The preceding results apply only to magnets whose length is very great in proportion to their transverse dimensions, and in which the form is perfectly regular—that is, prismatic or cylindrical, and the magnetisation likewise regular: in lozenge-shaped needles, the poles are much farther from the extremities.

MAGNETIC INDUCTION.

It has already been mentioned that a piece of iron or steel placed in contact with a pole of a magnet, either natural or artificial, becomes itself a magnet. This action likewise takes place, though with diminished intensity, at a distance, and is not prevented by the interposition of non-magnetic bodies. This effect is called magnetic induction, and the law according to which it takes place is precisely analogous to that of electric induction (ii. 384), viz. that *The extremity of the iron or steel nearest to the inducing magnetic pole, becomes a pole of contrary name, and the farther extremity a pole of the same name as the inducing pole.* Thus, suppose a bar of soft iron to be placed in contact with the north pole of a magnet; on presenting a magnetic needle to its farther extremity, the needle will turn its south pole to the bar, showing that that end has become a north pole. If the bar be detached and the inducing magnet removed, the polarity of the bar is immediately destroyed, and the needle returns to its normal position; and if the south pole of the magnet be now placed contact with or near to the end of the bar, the needle will turn round and present its north pole to the farther extremity. The polarity of the end of the bar which is in contact with the inducing magnet, cannot easily be tested in a similar manner, on account of the contrary action of the inducing pole; but if a short steel bar be substituted for the soft iron, and left in contact with the magnet for a few seconds, it will, on being separated, exhibit two poles, that which has been in contact with the pole of the inducing magnet being a pole of contrary name.

Moreover, the iron or steel thus rendered magnetic by induction will act in a precisely similar manner on any other piece of iron or steel in its neighbourhood, developing polarity in it, if previously unmagnetised, and altering the distribution and intensity of its polarity if previously magnetised. Consequently, just as the electric polarity of a charged body is intensified by developing electricity in a neighbouring conductor (ii. 385) so likewise may the polarity of a magnetic bar be strengthened by inducing magnetism in a neighbouring piece of iron. Thus, suppose a bar of soft iron, B, to be placed in contact with the north pole of a steel magnet, A, in the manner represented in *fig.* 722, B will then become a magnet with its poles disposed similarly to those of A, and will act upon A, just as if B were the original magnet, and A the unmagnetised iron. The original polarity of A will therefore be strengthened; and, in fact, it is found that a steel magnet is rendered more powerful and capable of supporting a greater weight, by leaving pieces of soft iron in contact with its poles.

Fig. 722.



It will be easily understood, from the preceding explanations, that the attraction of unmagnetised iron by the magnet is not an isolated phenomenon, but merely a particular case of the general law of the attraction between similar magnetic poles. This is also easily shown by experiment. Suspend a piece of iron, a key for example, from the north pole of a bar magnet; then bring the north pole of a second magnet in contact with the first; the key will be held with greater force than before, because the two magnets polarise it in the same way. Now turn the second magnet round, and bring its south pole in contact with the north pole of the first; the key will immediately drop off, because the second magnet induces in it a polarity contrary to that of the first, and reduces it to the condition of unmagnetised iron.

The case is, however, different if the two magnets act at opposite ends of the unmagnetised iron. Thus, let two magnetic poles P, P′, (*fig.* 723) be brought in contact with the two ends of a bar of soft iron B, not more than two or three inches long. If the poles P, P′, are similar, the iron will not be held up by them, because they tend to polarise it in opposite ways; but if the poles P, P′ are dissimilar, their polarising actions will conspire, and the piece of iron will be held up with greater force than it would be by either of them alone. Hence also a magnet bent in the form of a horse-shoe (*fig.* 724) will hold a piece of iron placed across its poles, with greater force than a bar magnet of the same size and intrinsic magnetic force; and by uniting a number of such horse-shoe magnets with their similar poles together, great power may be obtained.

Fig. 723.

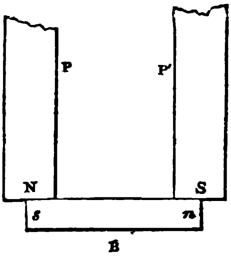
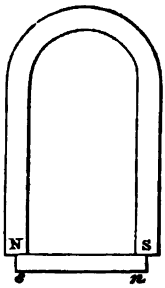


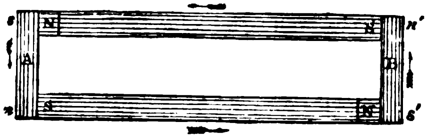
Fig. 724.



Another fact tending to show that the attraction of iron by a magnet must be preceded by magnetisation of the iron is, that very hard steel, which acquires polarity but slowly is scarcely attracted by the magnet.

It is easy to see that the poles *s*, *n*, of a piece of iron laid across the poles of a horse-shoe magnet will strengthen its polarity; in fact it is the constant practice to keep horse-shoe magnets, when not in use, with a piece of soft iron—thence called a keeper—across their poles. In like manner the best way of preserving the power of bar magnets is to lay two of them side by side in a box, with their poles pointing opposite ways and with keepers placed across them (*fig.* 725).

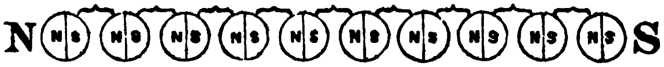
Fig. 725.



Molecular Constitution of Magnets.

All the magnetic phenomena hitherto considered are consistent with the supposition that the north polarity resides in one half of the magnet, and the south polarity in the other, each kind of polarity gradually increasing in intensity from the median line to the ends. But there are certain effects which show that magnetic, like electric power, resides in molecules, not in masses. Take a steel wire regularly magnetised, and break it in the middle. It will be found that each half is a complete magnet, having a north and a south pole, with a median line between them; and if each half be again divided in the middle, four complete magnets will be obtained, each having a north and a south pole, and so on, to whatever extent the division may be carried. This result is easily intelligible, if we suppose the original magnet to be a collection of molecules, each having a north and a south pole, and all the similar poles pointing the same way. It is easy to see that, in such a row of particles, as in *fig.* 726, the opposite polarities towards the middle of the series will neutralise one another, and only those of the two extremities will be perceptible; but that, if the series be divided at any point, each half will exhibit polarity similar to that of the whole. That such a series of polarised particles really acts like an ordinary magnet, may be shown by partly filling a glass tube with steel filings, and passing the pole of a strong magnet five or six times along the outside of it in one constant direction, taking care not to shake the tube. The individual filings will thus be magnetised, and the whole column, if presented to a magnetic needle, will attract and repel its poles, just like an ordinary bar magnet, exhibiting a north pole at one end, a south pole at the other, and no polarity in the middle; but on shaking the tube, or turning out the filings and putting them in again, so as to destroy the regularity of the arrangement, every trace of polarity will disappear.

Fig. 726.



It is necessary, however, to observe that, in a single row of particles, such as that in *fig.* 726, each possessing equal magnetic polarity, the resultant polarity would be exhibited only at the very extremities. Now, this is not what is actually observed in magnets; and the difference must be attributed to the lateral actions of the particles in the several rows composing the magnet, one on the other.

Processes of Magnetisation.

From what has been said of the molecular constitution of magnets, it is clear that the process of magnetisation must consist in polarising each separate molecule of which the bar is composed. Now, when a bar of soft iron is placed in contact with a magnetic pole, the nearest particles become polarised by the direct influence of that pole, these polarise the next, and thus the polarisation is rapidly developed all along the bar. But hard iron and steel offer a certain resistance, called the coercive force, to the polarisation of their molecules, so that the development of magnetism in them, especially in steel, is slower in proportion to the hardness of the temper. Thus, when a bar of hard steel is placed in contact with the north pole of a magnet, the nearer extremity immediately becomes a south pole, but the farther end shows no polarity at first. A north pole is, however, formed at a short distance from the south, and near this another weak south pole, just as if the bar were divided at that point, and the portion of it first polarised acted like a separate magnet on the portion beyond. These poles gradually advance along the bar, a feeble south pole appearing after a while at the farther end, succeeded, after a while—if the bar is not too long—by a north pole, the bar then appearing regularly magnetised. If, however, the bar is very long, and made of very hard steel, it never attains this regular magnetisation, but exhibits a series of alternate or *consecutive* poles, which never reach its farther extremity. The coercive force may, however, be more or less overcome, and regular magnetisation facilitated, by striking the bar with a piece of metal, so as to make it ring, and throw its particles into vibration.

It is obvious that the polarisation of the whole series of particles composing the bar will be accelerated by laying it between two bar magnets, with their opposite poles facing one another, or across the poles of a horse-shoe-magnet, the magnetisation then taking place in two directions at once, and both tending to the same result.

Another process more generally adopted, consists in passing the pole of a magnet from one end to the other of the piece of steel to be magnetised, repeating the friction several times and always in the same direction. Each particle of the steel is then brought successively under the influence of the magnet, and it is found that the magnetic power of the bar increases with the number of strokes up to a certain point, after which no further increase takes place. The polarity imparted to each particle as the magnetic pole approaches it, is reversed when the pole passes over it, so that the polarity finally imparted to the bar is that which corresponds to the last position of the inducing magnetic pole. If, for example, the steel bar be rubbed with the north pole of a magnet, the end first touched will be a north, and the other end, by which the magnet leaves the bar, will be a south pole. It is not very easy to understand what is gained by repeating the friction, inasmuch as the polarity imparted by each stroke is reversed at the commencement of the next. Possibly the coercive force of the steel is overcome by the disturbance consequent on the continued reversal of the polarity, much in the same manner as it is by vibration.

Greater power may be obtained by a combination of the two methods above described namely, by laying the bar to be magnetised between the opposite poles of two magnets, or those of a horse-shoe-magnet, then, taking two other bar magnets, one in each hand, bring down their opposite poles on the middle of the bar to be magnetised, and keeping them at an inclination of 25° or 30°, draw them outwards, with a regular motion, towards the extremities of the bar. Ten or twelve strokes given in this manner, and always in the same direction, will give to the bar, if not very large, as much magnetic power as it is capable of retaining. It is of course necessary that the pole of each movable magnet which touches the bar, should be of the same name as that of the fixed magnetic pole towards which it is made to move. This method, invented by Duhamel, and called the *method of single touch*, is the best for magnetising compass needles, and bars of no great length and thickness, in which regular distribution of magnetism is desired rather than great attractive power; but for magnetising long, thick bars, especially when it is desired to give them their full power, the following method of Æpinus, called the *double touch*, is to be preferred. The bar is laid between two powerful magnets as in the preceding method, and likewise rubbed with the opposite poles of two magnets; but instead of drawing these poles from the middle towards the opposite ends of the bar, they are tied together, with a piece of cork or wood between them to keep them at a certain distance apart, and made to travel together along the bar, first one way and then the other, beginning and leaving off in the middle. A horse-shoe-magnet may be conveniently used instead of two bar-magnets tied together. By this method it is likewise easy to magnetise two steel bars together, namely, by placing them parallel to one another, with soft iron keepers across their extremities, as in *fig.* 725, and passing the two magnetic poles several times round the rectangle thus formed, beginning in the middle of one of the bars, and leaving off at the same place. In this, as indeed in all methods of magnetising, the bars, after having been rubbed a certain number of times on one side, should be turned round and rubbed in the same manner on the other.

In both these methods, when two movable magnets are employed, the polarity which any particle acquires while outside the magnetic poles, is reversed when by their motion it is brought between them. Now the advantage of the double touch method consists in this, that the two poles of the movable magnet or magnets are separated by only a small distance, so that the sum of their actions on a particle between them is made as great, and the difference of their actions on an outside particle as small, as possible. This very circumstance, however, by developing powerful magnetism at once in a particular part of the bar, creates a tendency to the formation of consecutive poles when the steel is very hard. Hence, as already observed, the single touch method is usually adopted where regularity of magnetisation is the main object in view.

Magnetisation by the Electric Current.—Very great magnetic power may be developed in soft iron by placing it within a long coil of wire through which an electric current is passing (ii. 448). Steel bars may be magnetised in the same way, but the magnetism thus developed in them is but feeble, apparently because there is a want of vibratory movement to overcome the coercive force. The magnetisation may indeed be facilitated, as in other cases, by striking the bar so as to make it ring while it is under the influence of the current; but the best mode of magnetising steel bars by the electric current, is to pass the bar through a short movable coil of wire, then fix it between two soft iron electro-magnets, the coils of which are connected with the movable coil, so as to form one continuous circuit, and, having made the connection with the battery, pass the movable coil backwards and forwards along the whole length of the bar, rubbing it at the same time against its surface, so as to excite a vibratory motion in the particles. In this way very powerful and regular magnetisation may be obtained (Daguin, *Traité de Physique*, iii. 608). It is easy to see, however, that this mode of magnetisation requires rather complex apparatus, especially as, to develope powerful magnetism in soft iron requires a very long coil of wire passing several times round the bar, and consequently a powerful battery of several cells to overcome the resistance of the circuit. In most cases, therefore, the simpler methods of magnetisation by the single and double touch are found more convenient.

Magnetisation by Terrestrial Induction.—If a bar of soft iron, destitute of magnetism when placed horizontally, be held in the line of the magnetic dip, or in the vertical position, which in these latitudes does not differ greatly from it, its lower extremity will be found to have acquired north, and the upper, south polarity. On reversing the bar, the polarity will be also reversed, the lower extremity being still a north pole. This effect is due to the inductive action of the earth, the northern hemisphere of which acts, as already observed, like the south pole of an ordinary magnet.

A bar of hard iron or steel held in a similar position, does not immediately exhibit magnetic polarity, but on striking it several times with a key or a hammer, it becomes permanently magnetised with its north pole downwards. In this way, permanent magnets may be obtained without the use of other magnets or of the electric current. The effect on steel may be greatly augmented by resting it on a bar of iron held vertically, and striking both. Scoresby obtained powerful magnets by the following method: A large bar of iron was placed vertically and struck, and having thus acquired a certain amount of magnetic power, it was placed successively on each of two steel bars, 30 inches long, and one inch wide, these bars being also placed vertically and struck at the same time. Six smaller bars of steel 8 inches long and half an inch wide were then magnetised in a similar manner, by resting them vertically on one of the larger steel bars, and striking them, by which treatment they acquired in a few minutes considerable suspending power. Lastly, the six small bars were joined two and two by their opposite poles, by means of soft iron keepers, and rubbed with the others according to the double touch method. By this treatment they were found to be magnetised to saturation.

In consequence of the magnetic action of the earth, all bars of iron, such as railings, lightning conductors, &c., standing for a length of time in a vertical position, become permanently magnetised, their lower ends in the northern hemisphere acquiring north polarity. The magnetism of the native black oxide of iron has doubtless been produced by the same causes, the very different magnetic power exhibited by different specimens being partly attributable to the different positions of the veins of ore with regard to the line of the magnetic dip, that is to say, the line of the resultant of the terrestrial magnetic forces.

Circumstances which influence the Power of Magnets.

Whatever may be the process of magnetisation adopted, there exists, for each bar or needle, a limit of magnetic force which cannot be permanently exceeded; this limit, which is called the point of saturation, depends essentially on the coercive power of the iron or steel of which the bar is made.

Steel bars may, however, be magnetised beyond their point of saturation, and do not return to it immediately, the time occupied in returning to it depending upon various circumstances, such as changes of temperature, the neighbourhood of other magnets, position with regard to the earth, &c. To ascertain whether a bar has been magnetised to saturation, it is sufficient to remagnetise it, in the same direction, with magnets stronger than those which were used in magnetising it originally; if it thereby acquires but little increase of power, and this power disappears after a while, we may conclude that the point of saturation had previously been attained.

Influence of Size and Shape.—With regard to size, Coulomb found: 1. That the magnetic moments of saturated magnets of the same substance and of similar form are nearly proportional to the cubes of their like dimensions. 2. That, in cylindrical needles of the same length, the magnetic power is sensibly proportional to the diameter. 3. The time of oscillation of a bar having a rectangular section, whose breadth is l, thickness e, and length 2L, is given by the formula:

$$t = me\sqrt{l} + nL,$$

in which m and n are constants, depending on the nature and hardness of the steel.

With regard to form, Coulomb found that thin lozenge-shaped bars have a greater *directive force* than rectangular needles of the same weight, thickness, and hardness.

Influence of Hardening and Tempering.—Coulomb, having magnetised a steel bar to saturation, after hardening it to different degrees, and testing its power by the method of oscillations, obtained the following numbers:—

Temperature of hardening	875°	975°	1075°	1187°
Time of 10 oscillations	93″	78″	64″	63″

Steel does not undergo any sensible modification of structure when hardened at temperatures below 870°, and accordingly the magnetic results are the same at all degrees of hardening below this limit; but when hardened at about 1100°, the steel is capable of acquiring double the magnetic force which it retains when hardened at lower temperatures: for the time occupied by the ten oscillations being 63″ instead of 93″, the magnetic forces are inversely as the squares of these numbers, that is as 3969 to 8649.

A steel bar hardened at a cherry-red heat, and then magnetised after having been tempered at different degrees, gave the following results:

Tempering heat	15°	267°	512°	1122°
Time of 10 oscillations . . .	63″	64·5″	70″	93″.

Hence it appears that the magnetic force is less in proportion as the steel is more tempered, the coercive force in fact diminishing with the hardness.

Very different results were obtained with thin and very elongated laminæ or needles. By magnetising them at different degrees of hardness, Coulomb found that when hardened at a white heat, they did not retain a higher degree of magnetic power than after having been completely tempered. In proportion as the hardness was diminished by tempering, the magnetisation became stronger, down to the tempering produced by a dull red heat. On tempering them still more, the directive force which they were capable of receiving continually diminished. Biot explains this anomaly by the formation of two consecutive poles in very elongated and strongly hardened needles, each half of the needle thus possessing two poles of contrary name, whereby the directive force is greatly lessened. But as the hardness is diminished, the poles nearest to the centre approach continually nearer to it, and finally disappear altogether.

Compass needles are usually tempered at the blue, that is to say, at about 300° C. In this state, the coercive force, though not at its maximum, is still very great, and the steel is less fragile than when more hardened, and less liable to acquire consecutive poles.

Nobili (Bibl. Univ. lvi. 82) has endeavoured to explain the influence of hardening on magnetisation by the inequality of density of the different parts of the hardened bar. He found that when a bundle of thin steel wires (about 50) was very strongly magnetised, and the wires separated a short time afterwards, each of them appeared strongly magnetised in the same direction; but when the bundle was made up again, and untied a few hours afterwards, several of the wires were found to be unmagnetised, and some had had their polarity reversed. Similar results had previously been obtained by Coulomb. It appears then that, in a system of parallel rows of magnetised particles, those which are most strongly polarised destroy or reverse the polarity of the weaker series, and determine the polarity of the whole, and if the original polarity of all the rows were equal, the magnetic power of the entire system would probably soon be extinct. Now a magnetised bar may be regarded as made up of concentric layers of polarised particles, and if the external shell is rendered denser than the interior by hardening, so that a larger number of magnetic elements are there included within a given space, this external shell will receive a higher degree of polarity than the external portions, and accordingly will neutralise their action and determine the polarity of the whole system. For the same reason soft iron which has been hammered or wire-drawn, acquires the power of retaining a certain portion of magnetism. According to this view, the coercive or retaining power does not depend upon any peculiarity in the physical or chemical constitution of steel, but is entirely due to the different densities of the superficial portions of its mass. This is in accordance with the fact that small bars are capable of retaining a proportionally greater power than large ones, their surface being greater in proportion to their volume. It is also supported by the following experiment made by Nobili. Two cylinders were constructed of the same kind of steel, and of equal length and diameter, but one solid, weighing 28 grms. the other hollow, weighing 16 grms. They were then hardened to the same degree, and both were magnetised to saturation. When placed at equal distances from a compass-needle, the solid cylinder deflected it 9½°, the hollow cylinder 19°. The great difference of power thus shown in favour of the hollow cylinder, the mass of which was not much more than half that of the other, appears to be due to the circumstance that it was hardened both within and without, and was therefore covered on both surfaces with the dense crust which, according to the preceding view, preserves the magnetic power, whereas the solid cylinder was thus hardened only at its outer surface. On the other hand, however, it must be admitted that this mode of explaining the retaining power of steel does not account for the known fact, that iron containing a small quantity of sulphur is capable of retaining magnetism, although perfectly homogeneous, and that very hard steel is scarcely if at all attracted by the magnet.

Influence of Heat.—The power of magnets is diminished by rise of temperature, temporarily or permanently according to the degree of heat applied. The effect of heat is to diminish the coercive force; and at a red heat, as first observed by Gilbert, a steel magnet loses the whole of its power. When, on the other hand, a magnet is only slightly heated, its power suffers only a temporary diminution, the original intensity being regained on cooling. This circumstance must be attended to in estimating the relative intensities of the earth's magnetism at different localities, by observation of the oscillations of a magnetic needle, as, if the temperature is higher at one place than at the other, allowance must be made for the diminution of magnetic intensity in the needle thereby produced.

On the other hand, magnetism is more easily imparted to steel at high temperatures; so that a bar may be very powerfully magnetised by placing it while red hot between the opposite poles of two strong magnets and cooling it quickly in that position. A steel bar heated to redness and then hardened by sudden cooling in the vertical position retains the magnetism imparted to it by the inductive action of the earth.

Coulomb has measured the decrease of the magnetic force of a bar as its temperature is raised. He first tempered the bar so that its coercive force should not vary during the heating, then having magnetised it and heated it to various temperatures, he obtained the following results:

Temperatures . . .	15°	50°	100°	264°	425°	637°	850°
Time of 10 oscillations .	63"	97·5"	104"	147"	215"	290"	very great.

According to Kupffer, the effect of heat upon a magnet is not instantaneous, but requires a considerable time to produce the utmost diminution of power of which it is capable. For example, on plunging a magnet several times into boiling water, and leaving it each time for ten minutes, a diminution of the magnetic force took place at each immersion up to the sixth, after which the power remained constant. Kupffer has also shown that when one half of a magnet is heated, that half becomes weakened, and the median line approaches nearer to the opposite end. According to Christie, the greater part of the diminution of the force of a magnet by heat takes place instantaneously, a result which is in accordance with the accumulation of magnetic power near the surface (p. 767).

Influence of Mechanical Actions on the Magnetic Power of Iron.

We have already had occasion to notice the influence of friction, percussion, and other causes which agitate the particles of bodies, in diminishing the coercive power of iron and steel, thereby weakening the power of permanent magnets, and facilitating the development of magnetism by induction. Various other mechanical actions which produce a temporary alteration in the molecular condition of a mass of iron, likewise produce a temporary alteration in the magnetic power which may be induced in it by any cause, the iron regaining its original magnetic power as soon as the disturbing force ceases to act.

Torsion.—The easiest way of examining the effect produced by torsion on the magnetic state of iron is that devised by E. Becquerel, which consists in making use of the currents excited in a helix enveloping the magnet, by every increase or diminution of its magnetic power (ii. 451). For this purpose, a wire of well annealed iron, stretched by a weight, is passed through a vertical glass tube, round which is coiled a helix in connection with a delicate galvanometer. The wire in this position becomes magnetised by the inducing action of the earth, and it is found that, on twisting it either way, the galvanometer needle is deflected, in a direction which shows that the magnetic power of the wire is diminished by the torsion; and when the wire is untwisted, the needle moves in the contrary direction, indicating that the magnetic polarity of the wire is returning towards its primitive state. On allowing the wire to oscillate freely by torsion, and interposing in the electric circuit a commutator which changes the direction of the current through the galvanometer every time it is reversed in the helix, that is to say, at the moments when the wire passes through the position of equilibrium and of maximum torsion, a continuous current may be obtained.

Wertheim has made numerous experiments on the relations between magnetism and torsion, by a method similar to that of Becquerel, using however a horizontal bar of iron enveloped by two helices, one formed of thick wire to receive the current which magnetises the bar, the other of a long thin wire to receive the induced currents and convey them to a galvanometer. The helices are placed near the ends of the bar, and occupy but a small portion of its length. Having first shown that the softest iron always possesses a certain amount of coercive power, and therefore always retains a certain amount of the magnetic polarity once induced in it, Wertheim obtained the following results:—1. Torsion and detorsion do not by themselves develope any magnetism in iron: for on placing the bar at right angles to the magnetic meridian, and twisting it, no induced current is developed.—2. If the bar is placed in the magnetic meridian, or subjected to the action of a magnet placed on the continuation of its axis or to the action of the electric current, the magnetising action of either of these causes is accelerated both by torsion and by detorsion; but when once the magnetic equilibrium is established, torsion weakens the total magnetisation, and detorsion restores it to its former amount: hence the maximum of magnetisation takes place in the state of *mechanical equilibrium*.—3. If the bar is withdrawn from the action of the magnetising agent, repeated torsion and detorsion quickly destroys the excess of temporary magnetisation, but continues to act indefinitely on the permanent magnetisation, which is diminished by torsion and restored by detorsion.—4. When the bar is in any given condition of magnetic equilibrium, all the effects of torsion are proportional to the angles of torsion; but the magnitude of these effects appears to depend much more upon the permanent magnetisation, than on the temporary magnetisation produced by the external cause.—5. The form of the section of the bar does not appear to exert any influence, but the deflections increase with its area and with the intensity of the magnetisation.—6. The order of the effects produced is the same for all kinds of iron, the only difference being in the absolute intensities of those effects. The hardest iron requires the greatest number of torsions and detorsions, to bring it to its condition of magnetic equilibrium, indicated by the equality of the opposite induced currents.—7. Steel also, the more it is hardened, requires a greater number of torsions and detorsions to bring it to a state of magnetic equilibrium; but when once this equilibrium is established, it cannot, according to Wertheim, be modified by torsion and detorsion alone, as is the case with iron. Matteucci, on the other hand, always obtained feeble currents in this case, these currents being weaker as the steel was more hardened. Hard iron exhibits an anomaly which has not been explained, the modification produced in it by torsion being greater immediately after the interruption of the magnetising current than during its passage. In this case, the diminution does not take place till after some time.

When the bar is in a state of temporary or permanent torsion before magnetisation, similar results are obtained; that is to say, the magnetic maximum corresponds, not with the initial state of torsion, but with that which exists in the state of mechanical equilibrium; so that the magnetism increases when the bar is twisted in the direction which diminishes the primitive torsion, and diminishes when the original torsion is re-established. But if the initial permanent torsion is produced while the bar is under the action of the magnetising current, a *rotation of the maximum* is observed; that is to say, the maximum is displaced, and in the direction of the torsion, the angle of rotation being greater as the iron is harder, and the permanent torsion greater. This angle is always less than half the temporary torsion which necessarily takes place during the production of a permanent torsion.

For further details on this subject, and on the reciprocal influence of magnetism on torsion, see **Wiedemann** (*Galvanismus und Electro-magnetismus*, ii. 430–449).

Traction and Flection.—According to **Matteucci**, a sudden elongation produced by tension in a wire of iron or steel, while subjected to the magnetising action of an electric current, produces an *increase* in the magnetic force, and a sudden shortening diminishes it. These results have been confirmed by **Wertheim**, who has also shown that *flection* and *deflection* act in the same manner as torsion and detorsion. All these effects are due to the displacements of the molecules produced by these various forces, whereby they are enabled to arrange themselves, either in the position most favourable for magnetisation, or the contrary.

Wertheim finds, in the increase of the magnetic capacity of iron by traction, an explanation of the well-known fact, that a magnet while loaded becomes continually stronger, but returns to its primitive state as soon as the weight is removed. He also attributes the great irregularities of the compass in large iron ships to the inevitable flections of the iron which take place during the voyage, these flections producing changes in the magnetisation of the iron, of which the *compensators* (p. 780) are unable to take account. These phenomena are the converse of those observed by **Joule** (Phil. Mag. xxx. 76 and 225), who found that an iron bar increases in length when magnetised under ordinary circumstances, but contracts if already powerfully stretched by a mechanical strain previous to magnetisation.

Magnetism compared with Electricity.

The phenomena of magnetic induction, above described, are analogous in almost every particular to those of static electric induction; but there is one essential difference between the two: *there is no such thing as magnetic discharge.* In the case of electrified bodies, we know that, when the opposite polarities of the neighbouring surfaces attain a certain degree of intensity, discharge takes place between them in the form of a spark; and the distribution of the electric forces, after this discharge, is no longer the same as before, the one body appearing to have lost a certain amount of power, and the other to have gained it (ii. 385). But in magnetic induction, nothing of the kind is observed. Whatever may be the power of a magnet, and however intensely a piece of soft iron may be polarised by contact with it, the iron can take nothing from the magnet; but as soon as the contact is broken, the soft iron loses its polarity, and the steel magnet is found to have lost nothing, but rather to have had its polarity intensified. Neither does hard iron or steel, though it remains magnetised after separation, take any power from the original magnet, its retention of polarity being in fact analogous, not to the condition of a body which has been electrified by discharge, but to a non-conducting body like sealing-wax, which has been electrified merely by induction, and then removed from the neighbourhood of the inducing body.

The phenomena of magnetism are not then precisely analogous to those of static electricity, notwithstanding the exact parallelism which exists between the two up to a certain point. But, as already explained under ELECTRICITY (ii. 447), the laws of magnetic attraction and repulsion are exactly similar to those of the mutual action of electric currents. Two helices of copper wire, through which electric currents are passing, attract and repel one another exactly like magnets, and, accordingly, all the phenomena of magnetic attraction and repulsion may be accounted for, if we assume that a magnet consists of an aggregate of particles having electric currents constantly circulating round them in one direction. This theory has been sufficiently developed in the article referred to, and we need not dwell upon it further.

But, as a bar of iron or steel is rendered magnetic by the action of an electric current passing near it at right angles to its length, we must suppose, if this theory be true, that an electric current has the power of inducing in magnetic bodies a system of electric currents in the same direction as itself; moreover, that these currents, once established, will continue, in soft iron, as long as the original current continues to act, and, in the case of steel, even after it has ceased. Now, this is not what is observed to take place in the action of electric currents on conducting bodies in general. We know that when a conducting wire forming a closed circuit is placed near another wire conveying an electric current, the latter, at the instant when it begins to flow, induces, in the first wire, a current opposite in direction to itself, this current, however, being merely instantaneous, and no induced current being perceptible so long as the inducing current continues to flow with uniform strength; and, finally, that when the original current ceases (or the battery circuit is broken), another momentary current passes through the second wire in the same direction as the inducing current. These effects of electrodynamic induction are evidently totally different from those which must be supposed to take place in magnets, according to Ampère's theory; and we must, therefore, suppose that magnetic bodies have a peculiar molecular constitution, which enables an electric current passing near them to excite continuous currents round their particles in the same direction as its own; or rather, perhaps, that these currents pre-exist in all magnetic bodies, even before the development of magnetic polarity, but are disposed without regularity, so that they neutralise one another; and that magnetisation, either by an electric current, or by another magnet, is the process by which these molecular currents are made to move in one direction (ii. 448).

The hypothesis that the molecules of magnetic bodies, such as iron and steel, are encircled by continuous closed currents of electricity, which, before the development of magnetic polarity, circulate indiscriminately in all planes, but, in a magnetised bar, circulate in such a manner that, on the whole, the prevailing direction of rotation is in the same direction as that of the hands of a watch conceived as situated at the centre of the bar, with its face towards the south pole and its back towards the north pole, and in a plane perpendicular to the line joining the two poles: this hypothesis accounts for all the most important facts connected with magnetisation, and receives from some of them a striking confirmation. According to this view, magnetisation consists in giving to the particles of a piece of iron such an arrangement that the prevailing direction of its molecular currents shall be that indicated above. Coercive force is, on the same view, a resistance to the motion of the particles, which requires to be overcome equally to produce magnetisation or demagnetisation; and the saturated state of a magnet is when the greatest possible number of molecular currents circulate in the same direction, with their axes parallel to that of the magnet.

That magnetisation is really attended by molecular motion is proved by the emission of musical sounds by a piece of soft iron which is suddenly magnetised or demagnetised, when it is so supported that the greater part of its mass is free to vibrate. The magnetic effects developed by torsion likewise show the intimate connection between molecular motion and magnetisation. This view also enables us to see why the coercive force of steel is increased by hardening; for the hardness of steel is nothing more than the result of the great resistance which its molecules oppose to mutual motion. The difference between the molecules of soft iron and those of steel with respect to magnetisation, may be regarded as analogous to that presented by a very finely hung magnetic needle and one that is coarsely hung, when a magnet is brought near them. The finely hung needle is immediately and completely turned from its normal position on the approach of the magnet, and at once returns to it when the magnet is removed: the coarsely suspended needle, however, is at first much less affected by the magnet, and does not turn to the full extent until the friction of its point of support is overcome by [illegible] gentle tap or shake, and, similarly, when the disturbing magnet is taken away, it does not return completely to its first position without the same aid. This comparison may serve to explain the influence of a blow or vibration in facilitating the magnetisation or an unmagnetised steel bar, and in weakening the force of a saturated steel magnet.

Universality of Magnetic Action—Diamagnetism.

Magnetism was for a long time regarded as peculiar to a small number of bodies, namely, iron, nickel, cobalt, and certain of their compounds; but later researches have shown that all bodies are more or less susceptible of magnetic influence, though they are not all affected in the same way. The question of the universality of magnetism was raised as early as the beginning of the eighteenth century. **Muschenbroek** and **Nollet** found that a large number of bodies in the state of powder, the ashes of plants, and small fragments of organic substances, were attracted by the magnet; but they attributed the result to the presence of small quantities of iron in the substances examined. The subject was also investigated by **Lehmann** and **Cavallo**; and **Brugmanns**, in 1778, observed that bismuth is *repelled* by the poles of powerful magnets,—a remarkable discovery, which did not receive at the time the attention it deserved. **Coulomb**, in 1802, found that fine needles of gold, silver, and other metals, also of glass, and of various vegetable and animal substances, suspended by a thread of unspun silk between the opposite poles of two powerful magnets, oscillated till they came to rest in a line between the poles; but he also showed that a very minute quantity of iron, not exceeding $\frac{1}{133,120}$, intimately mixed with a needle of wax, was sufficient to produce this effect: hence he considered it uncertain whether the effects observed were due to the action of the magnets on the various substances themselves, or on minute quantities of iron contained in them. After the discovery of electro-magnetism, **Becquerel** observed that rods of shellac, wood, and other substances, suspended by threads of unspun silk within the coil of a galvanometer, placed themselves with their axes *parallel* to the plane of the coil, instead of at right angles to it, as an iron needle would: this effect was exhibited in a remarkable manner by a paper tube filled with ferric oxide. **Lebaillif**, in 1828, found that a delicately suspended magnetic needle was repelled by bismuth and antimony, thus confirming the important observation previously made by Brugmanns. The same kind of repulsive action was subsequently observed by **Saigey** in several other substances.

But these facts, however important they may now appear, excited but little attention at the time of their discovery, inasmuch as they could not be referred to any general law; and the question of the universality of magnetism remained undecided, until **Faraday**, in 1845, discovered that most transparent substances, when subjected to the influence of powerful magnets, acquire the power of circular polarisation (p. 676); and regarding this effect as resulting from the action of the magnet on the molecules of the transparent body, he was led to undertake a series of researches which resulted in the grand discovery, that all bodies whatever are subject to magnetic influence, but are not all affected by it in the same way, being divided, with respect to their magnetic susceptibilities, into two great classes—the *Magnetic* and the *Diamagnetic*. The former class includes those bodies which exhibit the well-known phenomena of ordinary magnetic attraction and repulsion—being *attracted*, when in their natural state, by either pole of a magnet, and, when shaped into bars or rods, and suspended joining two opposite magnetic poles, pointing *axially*—that is to say, in a straight line between them. The bodies belonging to this class are mostly metallic (including oxides and salts), viz. iron, nickel, cobalt, manganese, chromium, cerium, titanium, palladium, platinum, osmium. The magnetic properties of iron, nickel, and cobalt have long been known.

In the other metals of the series, magnetic susceptibility can only be detected by the use of magnets of great power. Manganese, chromium, cerium, titanium, and osmium are placed by Faraday in the magnetic class, because certain of their compounds exhibit the ordinary magnetic relations.

The second or *Diamagnetic* class includes all liquids and solids, both organic and inorganic, which do not belong to the *magnetic* class. The law which governs the action of magnets on these bodies is as follows:—*A particle of a diamagnetic body placed in the neighbourhood of either pole of a magnet is* repelled *by that pole.* Hence, a bar of any diamagnetic substance suspended by its centre midway between two magnetic poles will point *equatorially*, that is to say, at right angles to the straight line joining the two poles—that being the position in which every part of it is at the greatest possible distance from each of the poles; and if its centre be placed on either side of the axial line, the whole bar will recede from that line, placing itself at the same time equatorially. A globe or cube does not *point*, but exhibits the simple phenomenon of repulsion. If two small balls of any diamagnetic substance be suspended between the two magnetic poles, they will be driven towards one another, as if they were actuated by mutual attraction. The position which a bar of any substance takes up when suspended horizontally between two magnetic poles furnishes the best means of determining whether it belongs to the magnetic or the diamagnetic class: if it be magnetic, it will place itself axially; if diamagnetic, equatorially.

The diamagnetic force cannot be perceptibly developed without the use of exceedingly powerful magnets: electro-magnets answer the purpose best, but large permanent magnets may also be used. The great power required to develope this mode of action accounts for its having been previously overlooked by most observers.

Bismuth appears to be the most powerfully diamagnetic of all substances; then follows phosphorus, then antimony, then heavy glass (silico-borate of lead). Among the metals, the order of diamagnetic energy appears to be as follows: bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, arsenic, uranium, rhodium, iridium, tungsten. (Faraday, *Experimental Researches in Electricity*, series 20 and 21; Phil. Trans. 1846, 21.)

Thallium is strongly diamagnetic, being nearly equal in that respect to bismuth. (Crookes.)

Air and other gases exhibit decided magnetic and diamagnetic relations. In his first experiments on this subject, Faraday was led to the conclusion that gaseous bodies were indifferent to magnetic action, forming the zero, or middle point, between the two classes of magnetic and diamagnetic bodies. Bancalari has, however, since discovered that flame possesses diamagnetic properties; and Zantedeschi has shown that air and other gases likewise exhibit diamagnetic relations. The researches of these Italian philosophers have been confirmed and extended by Faraday: the following are the principal results.

An arrangement was made by which a stream of any gas could be delivered in a vertical direction, either upwards or downwards, near the middle point of the axial line, between two powerful magnetic poles of opposite names, but at a short distance on one side of that line. By this arrangement it was found that the following gases were driven away from the magnetic axis and passed off in the equatorial direction; that is to say, they exhibited diamagnetic relations with regard to atmospheric air—nitrogen, hydrogen, carbonic anhydride, carbonic oxide, coal-gas, olefiant gas, sulphurous anhydride, hydrochloric acid, hydriodic acid, fluoride of silicium, ammonia, chlorine, nitrous oxide, and the vapours of bromine and iodine. Nitric oxide and pernitric oxide were also slightly diamagnetic in air. Oxygen was strongly magnetic—that is to say, it was drawn towards the axis, and then along it in opposite directions towards the two poles, round which it accumulated.

The first-mentioned gases evidently differed from each other in diamagnetic energy; but it was found impossible by the means above described to form anything like a precise estimate of their relative powers. To determine this point, the magnetic poles were surrounded with an atmosphere of one gas, while the other gas was directed in a vertical stream, either upwards or downwards, near the axial line as before. By this method it was found that (1) *In carbonic anhydride*, air and oxygen passed axially; nitrogen, hydrogen, coal-gas, olefiant gas, hydrochloric acid, and ammonia, equatorially: so likewise did carbonic oxide and nitrous oxide, but the action was feeble. (2) *In coal-gas*, air appeared magnetic, though but slightly; oxygen was strongly magnetic: nitrogen was strongly diamagnetic; olefiant gas, carbonic oxide, and carbonic anhydride, feebly so. (3) *In hydrogen gas*, air, when free from smoke, passed axially; but when mixed with smoke, it was either indifferent or passed equatorially. Hydrogen gas and atmospheric air seem to be not far removed from one another in the scale. Oxygen was strongly magnetic; nitric oxide also magnetic, but in a less degree. Nitrogen was strongly diamagnetic; nitrous oxide, carbonic oxide, carbonic anhydride, and olefiant gas were also diamagnetic; hydrochloric acid and chlorine slightly so. Oxygen appears to be the most magnetic of all gases.

When a spiral of platinum wire was placed just below the middle point of the axial line and ignited by a voltaic current, the stream of hot air which rose up against the axial line was deflected at right angles to the axis, and passed off in the equatorial direction. The same effect was obtained in oxygen, carbonic anhydride, and coal-gas. Hence it appears that a heated gas is diamagnetic to the same when cold. A stream of cold air directed downwards near the axial line, was drawn towards that line.

The flame of a wax taper or of burning ether also takes an equatorial direction when placed in or near the middle of the axial line. When placed a little on one side of the axis, it is directed away from that line, just as if a gentle wind were blowing upon it in that direction. When made to rise exactly in the axial line, it divides itself into two long tongues, directed at right angles to the axis. This effect is particularly striking with the large flame produced by setting fire to a ball of cotton soaked in ether. These effects are evidently analogous to those just described with hot air; but they are doubtless partly due to the solid carbonaceous particles in the flame, which are diamagnetic. In corroboration of this supposition, it is found that the brightest flames are the most strongly diamagnetic. (Faraday, Phil. Mag. [3] xxxi. 401: see also Zantedeschi, xxxi. 421.)

Specific Magnetism. This term was introduced by E. Becquerel, to denote the action exerted by a magnet on the unit of volume of a body placed at the unit of distance, as compared with that which is exerted on a certain substance taken as the standard of comparison. Another mode of estimation is to compare the effects produced on a small magnetic needle, by a cube, equal to the unit of volume, placed at the unit of distance from the needle. The measurements are made either by the torsion balance, or by determining the weight required to keep the body in a certain position of equilibrium while under the influence of the magnet.

By these methods, Plücker, representing the specific magnetism of soft iron by 100,000, has found for native magnetic oxide the number 40,227, for specular iron ore 533, for brown hæmatite 71, which is the lowest number found for any of the compounds of iron, solid or liquid.

The following are the results obtained by Plücker for certain *diamagnetic* substances at ordinary temperatures, and for equal weights referred to water as unit.

Specific Diamagnetic Powers. (Plücker.)

Water	100	1	Flowers of sulphur	71	$\frac{3}{4}$
Phosphorus	100		Common salt	70	
Sulphide of carbon	102		Nitric acid	48	$\frac{1}{2}$
Hydrochloric acid	102		Nitrate of bismuth	35	$\frac{1}{3}$
Ether	127	$\frac{5}{4}$	Sulphuric acid	34	
Oil of turpentine	123		Mercury	23	$\frac{1}{4}$

This table shows that the diamagnetic powers of different groups of substances may be approximately expressed by simple numbers; but it is doubtful whether this result is accidental, or expresses an actual law.

The following table contains some of the results obtained by E. Becquerel, the magnetic power of water being taken as unity, and the results referred to equal volumes Diamagnetic substances are denoted by the *minus* sign.

Specific Magnetic Powers. (E. Becquerel.)

Solids.	Specific magnetism in air.	Liquids.	Specific gravity.	Specific magnetism in air.
Water	−1·00	Water	1·0000	−1·00
Zinc	−0·25	Alcohol	0·8059	−0·97
White wax	−0·57	Ammonia	0·8059	−1·02
Melted sulphur	−1·14	Common salt	1·2084	−1·13
Copper (electrotype)	−1·41	Chloride of magnesium	1·3197	−1·21
Copper, pure	−1·68	Sulphide of carbon	1·3197	−1·33?
Lead, commercial	−1·53	Sulphate of copper	1·1265	+0·81
Phosphorus	−1·64	„ of nickel	1·0827	+2·16
Selenium	−1·65	Ferrous sulphate	1·1728	+18·02
Silver, pure	−2·32	„ „	1·1923	+21·12
Gold (nugget)	−2·41	„ chloride	1·0695	+ 9·19
Gold, pure	−3·47	„ „	1·2767	+36·07
Bismuth	−21·76	„ „ (concentrated)		
„	−22·67		1·4334	+65·01

To compare the magnetic powers of iron with water, and thence with other bodies,—which is somewhat difficult, on account of the very great disproportion existing between the two,—Becquerel made use of the concentrated solution of ferrous chloride, as an intermediate term of comparison. This solution, which has a specific magnetic power of + 658·13, that of water being − 10, was introduced into a tube of thin glass, 4 centimetres long, suspended between the contrary poles of two bar magnets, and its oscillations were compared with that of a bar of wax of the same length mixed with a known weight of soft iron filings. The numbers of oscillations made by such bars in a given time are independent of their bulk, and proportional to the quantity of filings contained in them. In this manner it was found that ferrous chloride experiences, for equal volumes, the same amount of action as an inert substance containing 0·2 milligr. of iron per cubic centimetre. Now, the magnetic power of water, compared with ferrous chloride, being $\frac{-10}{+658{\cdot}13} = -0{\cdot}0152$, will also be equal to that of an inert substance containing $0{\cdot}0152 \times 0{\cdot}2 = 0{\cdot}003$ milligr. of iron per cubic centimetre, but of contrary sign. Hence, as a cubic centimetre of iron weighs 7·758 grms., the magnetic powers of iron, ferrous chloride, and water are, for *equal volumes*, as the numbers + 1,000,000 : + 25·7 : − 0·4 ; and for *equal weights*, as + 1,000,000 : + 140 : − 3.

Faraday has also compared the magnetic powers of a considerable number of substances by the method of torsion. The next table contains some of his results for equal volumes *in vacuo*, and referred to water as unity. They were all obtained at the temperature of 15·5° C. (60° F.), and for gases under the pressure of 0·76 metre.

Specific Magnetic Powers. (Faraday.)

Substances.	Magnetic powers.	Substances.	Magnetic powers.	Substances.	Magnetic powers.
Proto-ammoniuret of copper	+ 1·309	Cyanogen	− 0·009	Ammonia (liquid)	− 1·010
		Glass	− 0·188	Sulphide of carbon	− 1·031
Per-ammoniuret of copper	+ 1·240	Zinc, pure	− 0·772		
		Ether	− 8·797	Nitrate of potassium (sat.)	− 1·036
Oxygen	+ 0·181	Alcohol (abs.)	− 0·815		
Air	+ 0·035	Oil of lemons	− 0·828	Sulphuric acid	− 1·081
Olefiant gas	+ 0·006	Camphor	− 0 855	Sulphur	− 1·221
Nitrogen	+ 0·003	Camphine	− 0·859	Chloride of arsenic	− 1·260
Carbonic anhydride	0·000	Linseed oil	− 0·886		
		Olive oil	− 0·886	Borate of lead (melted)	− 1·413
Hydrogen	− 0·001	Wax	− 0·887		
Ammonia gas	− 0·005	Nitric acid	− 0·911	Bismuth	− 20·369

A comparison of the specific magnetic powers of different elementary bodies shows that, in many instances, the most magnetic are those which have the smallest atomic volume (i. 442), or those whose atoms are the closest together; and that diamagnetic bodies, on the other hand, are those whose atoms have the largest spaces between them. Thus bismuth, the most diamagnetic of all bodies, has also a high atomic volume (21·2); whereas iron, nickel, and cobalt have very low atomic volumes, viz. about 3·5. But on the other hand, copper and zinc, which have also small atomic volumes, viz. 3·6 and 4·6 respectively, are slightly diamagnetic; and sodium and potassium, whose atomic volumes are larger than those of any other metals (sodium 23·7, potassium 45·6), are, according to Lamy, slightly magnetic. The relative distances between the atoms is, therefore, not the only, and perhaps not the principal, cause which determines the difference between magnetic and diamagnetic bodies.

No definite relation has yet been discovered between the magnetic or diamagnetic powers of compounds and those of their elements. It is known, however, that the compounds of iron are for the most part magnetic; but exceptions occur even among these, the ferrocyanide and ferricyanide of potassium, for example, being diamagnetic. The magnetic relations of atoms are, therefore, dependent to a certain extent on their state of combination.

The magnetic and diamagnetic powers of mixtures are, according to Matteucci, sensibly equal to the sum [? the mean] of those of their components.

Specific Magnetism of Oxygen and Air.—Matteucci has compared the magnetic power of oxygen with that of iron by the following method, which serves also to show, in a striking manner, that oxygen is magnetic:—A large bubble of oxygen is introduced into a tube filled with alcohol, and the tube is placed transversely between the hemispherical polar extremities of a very strong electro-magnet. If the bubble is placed tangentially to the polar line, it elongates towards this line; and if its centre is over the polar line, it shortens. If the alcohol is saturated with protochloride of iron, the bubble in the latter position splits into two, which move away from one another. By ascertaining by trial the proportion of ferrous chloride, for which the bubble experiences no perceptible change of form, a solution will be obtained, having the same magnetic power as oxygen gas. By this method Matteucci found that oxygen has the same magnetic power as an alcoholic solution of ferrous chloride containing three milligrammes of iron in a cubic centimetre.

E. Becquerel has made numerous experiments for the purpose of measuring the magnetic power of oxygen as compared with water, and thence with iron. A small tube of glass filled with wax was suspended from a torsion apparatus, and the effects produced upon it by an electro-magnet in a vacuum, in oxygen and water, were compared. These actions, at the temperature of 12°, were, *in oxygen* under a pressure of 0·76 met., $V_o = -0{\cdot}2675$; in a vacuum, $V_v = -0{\cdot}1145$; and in water, $V_w = +0{\cdot}7033$. Hence $V_o - V_v = +0{\cdot}1530$: $V_w - V_v = -0{\cdot}8178$; and the magnetism of *oxygen*, compared with water *in vacuo*, is $0{\cdot}1530 : 0{\cdot}8178 = 0{\cdot}1871$. Hence, for equal volumes, the magnetic power of oxygen is nearly $\frac{1}{5}$ of that of water, but of contrary sign. For *air* the same method gives the number 0·03771: hence, as the magnetic power of oxygen multiplied by 0·21 is 0·392, it follows that the magnetic power of the air is due to the oxygen contained in it. These results are nearly the same as those obtained by Faraday (p. 773) and Matteucci; and Becquerel has further confirmed them by Plücker's method. Lastly, he has shown that the magnetic power of oxygen is proportional to its pressure—a result probably true also for other gases.

Taking the magnetic power of iron as the standard, and calling it 1,000,000, we find that, for *equal weights*, the magnetic power of oxygen is 377, and that of air 88. Oxygen, *weight for weight*, has three times the magnetic power of ferrous chloride, which is the most magnetic of all liquids. Hence a cubic metre of oxygen gas would act on a magnetic needle with the force of 54 centigrammes of iron, and a cubic metre of air with the force of 11 centigrammes of iron. The whole atmosphere is consequently equal in magnetic power to a shell of iron covering the whole earth to the thickness of 0·1 millimetre. It is easy to conceive that such a magnetic envelope, in a state of constant agitation, is capable of disturbing the magnetic needle; and as its magnetic power varies with its temperature (see below), the heating which it undergoes at different hours of the day may contribute to produce the diurnal variations (p. 782).

Influence of Temperature on Magnetism and Diamagnetism.—The effect of heat on the magnetic power of iron and steel has already been mentioned (p. 767). It was formerly supposed that iron at a white heat becomes totally unsusceptible of magnetic influence. Faraday has, however, shown that, though the susceptibility of magnetic bodies properly so called is rapidly diminished by heat, it is never completely destroyed, but is still perceptible at the highest temperatures, provided that electro-magnets of great power are employed to develope it. These results have been confirmed by Plücker, who has shown that the specific diamagnetism and magnetism of solids and liquids diminish, for the most part, as their temperature is raised, but that there are some exceptions to the rule. Mercury, for example, exhibits no change of diamagnetic power at 300°; neither do sulphur and stearin, even when heated above their melting points. Brunner has shown that water in the state of ice and of vapour has the same specific magnetism as in the liquid state.

According to Matteucci (Bibl. Univ. de Génève [Arch. des Sc. xxiii.], 24), the magnetism of iron increases up to a certain temperature, then decreases rapidly. The diamagnetic power of bismuth diminishes between 0° and 212° C.—nearly in proportion to the increase of temperature, and vanishes altogether at the melting point. Non-metallic bodies, on the contrary, such as sulphur and phosphorus, scarcely suffer any diminution of diamagnetic power in consequence of change of state.

A globule of iron melted in a lime-spoon by the oxy-hydrogen blowpipe was still attracted by the magnet; but to exhibit the attraction, a very large electro-magnet was required, charged with 30 Grove's cells. Matteucci estimates the magnetic power of melted iron at only 0·000015 of its power at common temperatures: hence it is not surprising that iron at a white heat should have been found insensible to the attractive power of ordinary magnets. Copper, standard gold, zinc, porcelain, and certain kinds of charcoal, which according to Matteucci are magnetic at common temperatures, become diamagnetic when heated. Platinum remains magnetic in the state of fusion, its power appearing scarcely to have suffered any diminution.

Heat appears also to diminish the magnetic power of gases: thus Faraday found that heated air is repelled by the magnet when surrounded by cold air (p. 771). E. Becquerel, however, concludes from his experiments on oxygen, that heat does not act *directly* in diminishing the magnetic power of gases, the diminution observed being solely due to change of density.

Influence of Compression and Crystalline Structure on Magnetism and Diamagnetism.—Faraday observed that the position assumed by a bar of bismuth under the influence of magnetic forces, is affected in a remarkable manner by its crystalline structure; and that when a cubic crystal of the metal is suspended between the poles of an electro-magnet, a certain line, perpendicular to the principal cleavage-plane of the crystal (called by Faraday the *magne-crystallic axis*), tends to place itself axially between the poles, and in other parts of the field, tangentially to the magnetic curve passing through the point where the crystal is situated. Plücker also remarked that a plate of tourmaline cut parallel to its axis, and suspended between the poles of an electro-magnet with that axis horizontal, places itself with the axis in the equatorial position, although the crystal is magnetic, in consequence of the iron which it contains, and if suspended with the axis vertical, is attracted by either pole of the magnet. Hence he concluded that the axis is repelled by the magnetic poles, and that the repulsion thus exerted is more powerful than the attraction due to the magnetic properties of the mass. Calc-spar, on the contrary, which is diamagnetic, places itself with its principal crystallographic axis in the line between the magnetic poles: similar results are obtained with heavy spar and dioptase, which are magnetic.

These phenomena have been reduced to a general law by the researches of Tyndall and Knoblauch (Ann. Ch. Phys. [3] xxxv. 375; xxxvii. 76), who have shown that when the particles of a body are more closely packed in one direction than in others, this direction—other circumstances being the same—is the one on which the forces acting upon the body are exerted with the greatest energy, and consequently this line of direction places itself axially or equatorially between the poles of a magnet according as the body is magnetic or diamagnetic. Thus a cylinder of carbonate of iron made into a paste with gum, places itself axially, if of uniform density in all directions; but if the paste be strongly pressed between boards into a thin cake, a bar or needle formed out of it will place itself equatorially between the poles, even if its length be ten times as great as its breadth. Conversely, a bar formed of a paste of bismuth filings and gum, which places itself equatorially if of uniform density, will assume the axial position if the paste be compressed transversely to the length of the bar.

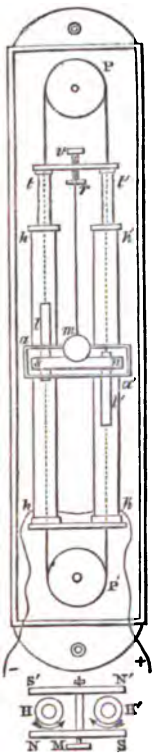
The effects observed in crystals of bismuth and other substances are of the same nature. That the molecular structure of crystals is not the same in all directions, is evident from their optical relations, their rates of expansion, and their heat-conducting powers; and the direction in which they place themselves under the influence of a magnet is determined by their relative densities in different directions, in the same manner as in the artificial structures above mentioned.

It is not, however, the direction of the axis of a crystal that ultimately determines the position which it assumes under the influence of a magnet, so much as that of the planes of cleavage, these planes taking the axial direction when the crystal is magnetic, and the equatorial if it is diamagnetic.

Thus, if two cubes be formed of the same dimensions, one from a crystal of beryl, the other from scapolite, both of which are magnetic, the former will place itself with its principal axis equatorially between the magnetic poles, the latter axially, because in beryl the cleavage-planes are perpendicular to the axis, whereas in scapolite they are parallel to it. Conversely, a cube of nitre, which is diamagnetic, places itself with the principal axis equatorial, whereas a cube of topaz, also diamagnetic, takes up the contrary position; because the cleavage-planes of nitre are parallel, and those of topaz are perpendicular, to the principal axis of the crystal. In all cases, the cleavage-planes place themselves axially or equatorially, according as the crystal is magnetic or diamagnetic. The manner in which this result is produced will be easily understood if we remember that a crystal may be regarded as an aggregate of very thin plates laid parallel to each other, but not in absolute contact. It is easy, indeed, to imitate the arrangement artificially. Thus, if a number of strips of emery-paper, an inch long and a quarter of an inch wide, be gummed together one upon the other, so as to form a rectangular bar, this bar will place itself axially between the poles of a magnet (the emery being magnetic); in fact, it represents a magnetic crystal having its cleavage planes parallel to the axis. But if another bar be formed, also an inch long, of square pieces of emery-paper, a quarter of an inch broad, having their surfaces transverse to its length, it will place itself equatorially, because, in that position, the layers of magnetic substance will take up the axial position. If the paper be covered with a paste of bismuth powder instead of emery, the effects will be exactly opposite.—*Traité d'Electricité*, par A. De la Rive (i. 516—529).

Diamagnetic Polarity. Soon after the discovery of diamagnetism, the question was raised, whether diamagnetic bodies possess opposite poles analogous to those of magnetic bodies. Faraday, from his earlier experiments, concluded that such was not the case, but that every part of a diamagnetic body was equally repelled by either pole of a magnet. On the other hand, Reich (Ann. Ch. Phys. [3] xxxvi. 127) found that a very delicately suspended ball of bismuth, though repelled by either pole of a horse shoe magnet, when presented to them separately, remained at rest when suspended at equal distances from the two: hence he concluded that the resultant effect of the two magnetic poles is due, not to the sum, but to the difference of their action, just as would be the case with the attractive actions exerted by the two poles on a ball of iron, and that the first effect of the magnet on the bismuth is to develope in it a certain polarity, whence results the repulsion. The question was likewise examined by Weber and Poggendorff, Plücker, H. C. Oersted, and Matteucci, but without decisive results, and the question as to the existence of diamagnetic polarity remained doubtful till it was taken up by **Tyndall** (Phil. Trans., 1855 and 1856), who, by means of an apparatus suggested by Weber, has completely established the existence of polarity in diamagnetic bodies.

Fig. 727.



This apparatus, represented in *fig.* 727, consists of two equal vertical helices, *h h*, *h'h'*, having an internal diameter of two centimetres, and coiled round copper tubes, which project above them at *t*, *t'*; these two helices convey the same electric current, but in contrary directions. They are fixed to a stout board suspended against a wall, and within them are suspended two small diamagnetic bars, *l*, *l'*, attached to an endless cord passing round the pulleys P, P'. An astatic needle, *sn*, represented in projection at N S, N' S', is suspended on a level with the middle of the helices *h*, *h*, by silk cords attached to the centre of a torsion-circle, *r*. This circle is capable of turning independently of the screw *v*, the nut of which is embedded in a copper cross-piece fixed to the extremities of the copper tubes *t*, *t'*. The magnets N S, N' S' are enclosed in a copper box, *a*, to diminish the amplitude of the oscillations; they are joined by a brass rod, on which they can be made to approach one another more or less.

The deflections of the astatic needle are observed by reflection in a mirror *m*, M, and measured by the reflection of a horizontal scale placed at a distance, as in Gauss's magnetometers. On transmitting a voltaic current from one or two Grove's cells through the two coils in opposite directions, the bismuth bars within them become diamagnetised; and by carefully raising or lowering the astatic bars N S, S' N', a position may be found in which the magnets become indifferent to the action of the current. If, whilst the apparatus is thus arranged, the wheel P be turned to the right, the bismuth bars will be brought into the position represented in the figure, and the astatic needle will be deflected. This effect is clearly due to the development of polarity in the bismuth bars: for, in consequence of the opposite direction of the currents on the two helices, the lower end of one bismuth bar will, if polar, be in the same condition as the upper end of the other, and each will therefore attract one particular end, say the north, of each magnet composing the astatic combination, and repel the south end: both bars therefore tend to deflect both magnets in the same direction; on turning the wheel to the left, so as to bring the bismuth bars into the opposite position, the needles will be equally deflected in the contrary direction.

These effects are most marked with bodies like bismuth and antimony, which have the greatest diamagnetic energy; but they are also distinctly shown, even in non-conducting bodies—such as heavy glass, phosphorus, sulphur, sulphide of carbon, &c.

If the deviation produced by solid bismuth be represented by 75 divisions of the scale employed, the following table will represent the action, found by Tyndall, of the other bodies enumerated in it:

Bismuth, solid	75	Heavy glass	4
„ powdered	37	Phosphorus	4
Antimony	13·5	Distilled water	4
Sulphide of carbon	5·5	Calcspar	2
White marble	5	Nitre	1·7

When *magnetic* substances, such as iron in bars or in filings, sulphate, carbonate, or chloride of iron, slate, solutions of salts of iron, nickel, or cobalt, are substituted for the diamagnetic bars, the astatic needles are deflected in the contrary direction to that in which, under the same circumstances, they would be deflected by diamagnetic bodies.

Theory of Diamagnetism. The phenomena of diamagnetism naturally suggest the inquiry, whether the repulsion exerted by a magnetic pole on diamagnetic bodies is a force distinct from that of magnetism, as exerted upon iron and other bodies of the magnetic class; or whether, on the other hand, the magnetic and diamagnetic conditions of matter are merely relative, so that all bodies are magnetic in different degrees, and the apparent repulsion of a diamagnetic body, such as bismuth, is merely the result of its being attracted by the magnet less than the particles of the surrounding medium, just as a balloon recedes from the earth, because its weight is less than that of an equal bulk of the surrounding air. It is easy to show that the same body may appear magnetic or diamagnetic, according to the medium in which it is placed. Protosulphate of iron is a magnetic substance, and water is diamagnetic: hence it is possible, by varying the strength of an aqueous solution of this salt, to make it either magnetic, indifferent, or diamagnetic, when suspended in air. Again, a tube containing a solution of protosulphate of iron suspended horizontally within a jar, also filled with a solution of the same salt, and placed between the poles of two powerful electro-magnets, will place itself axially or equatorially, according as the solution contained in it is stronger or weaker than that in the jar. In the same manner, then, we may conceive that bismuth places itself equatorially between two magnetic poles, because it is less magnetic than the surrounding air. But the diamagnetism of bismuth and other bodies of the same class shows itself in a vacuum as well as in air: hence, if diamagnetism is not to be regarded as a distinct force, we must suppose that the *ether* is also magnetic, and occupies in the magnetic scale the place intermediate between magnetic and diamagnetic bodies.

That a body suspended in a medium of greater magnetic susceptibility than itself, will recede from a magnetic pole in its neighbourhood, in consequence of the greater force with which the particles of the medium are impelled towards the magnet, is so obvious a consequence of mechanical laws, that we can scarcely avoid attributing the movements of diamagnetic bodies to the cause just mentioned, at least, when the body is suspended in air or other magnetic gas. There is, however, some difficulty in reconciling the phenomena exhibited by compressed and crystallised bodies (p. 774) with this view. Tyndall some time ago (Phil. Mag. [4] ix. 205) objected to it, that the intensity of diamagnetism as well as that of magnetism is increased by compression; whereas, if the repulsion of a diamagnetic body were merely the result of the greater attraction exerted upon the particles of the surrounding medium, it ought to be weakest in that direction in which the body is most compressed, inasmuch as the compression must increase the total amount of attraction exerted on the particles of the body in that direction, but cannot in any way affect that which is exerted on the surrounding medium. Williamson (Proc. Roy. Soc. vii. 306) has, however, pointed out that, in considering this question, it is necessary also to take account of the attraction exerted on the magnetic medium (or *ether*) interposed between the particles of the magnetic or diamagnetic body. When a cube of carbonate of iron is compressed, the ponderable particles being more magnetic than the medium which they displace, the force with which the body is attracted is increased proportionally to this excess. If it becomes more magnetic by compression, we must conclude that the loss of magnetic medium from its interstices is more than supplied by the magnetic matter which takes its place. Carbonate of calcium, on the other hand, is less magnetic than the quantity of medium which its particles displace; and when these particles are brought closer together by pressure, the mass becomes more diamagnetic, because a certain quantity of the magnetic medium is thus replaced by the less magnetic matter. In both bodies, so long as they retain their original crystalline forms, the optic axis is the direction in which the function of the ponderable particles predominates most strongly over that of the medium; so that in the iron-salt it is the strongest, and in the calcium-salt the feeblest magnetic direction of the crystal. On the other hand, Hirst (Proc. Roy. Soc. vii. 448) suggests that, in estimating the resultant action of a magnet on the particles of a body and the magnetic medium enclosed between them, account must be taken of the relative intensities of the action exerted on the medium in different directions: and he endeavours to show, by a process of reasoning for which we must refer to the paper above quoted, that, in two out of three possible cases, viz. (1), when the attraction of the magnet on the interposed medium is equal in all directions with regard to the line of compression, and (2) when it is greatest in that direction, the repulsion produced on a body whose specific magnetic susceptibility is less than that of the medium, will be a minimum in that direction; and, therefore, that in these two cases, the objection raised by Tyndall against the theory of diamagnetism under consideration is valid: but that, thirdly, in the somewhat improbable case in which the action of the magnet on the interposed medium is greatest in the direction at right angles to that of strongest attraction of the ponderable particles, the latter may be so far diminished, that the body may be most strongly repelled by a magnetic pole in the direction of greatest compression. If, therefore, this third case be also taken into account, Tyndall's objection to the theory of a magnetic medium cannot be regarded as perfectly decisive.

On the whole, then, the phenomena exhibited by compressed and crystallised bodies do not quite decide the question whether diamagnetic repulsion is merely a differential phenomenon, or whether it is due to the action of a specific force. That it is partly differential, can, as already observed, scarcely be doubted; but, on the other hand, the existence of diamagnetic polarity shows decidedly that the effect is not wholly due to this cause: for if it were, every part of a diamagnetic body would be repelled by either pole of a magnet.

It becomes necessary, therefore, to seek some further explanation of the phenomena of diamagnetism; and the following theory has been proposed by Weber and De La Rive. We must suppose, in the first place, that each molecule of a body possesses a natural polarity, by virtue of which, negative electricity tends to accumulate at a certain point, *c*, of its surface (*fig.* 728), and positive electricity at the opposite point, *b*. If this molecule is isolated and a good conductor, the two electricities will recombine along its surface, forming currents contrary to those which are continually being produced in its interior to re-establish the polar tension; and the actions which these currents would tend to produce on any external point, destroy one another. If now the molecule be supposed to make one of a group, all the atoms of this group will act upon each other so as to bring their contrary poles towards one another, as in *fig.* 729, and the opposite electricities, instead of recombining on the surface of each molecule, will form intermolecular discharges, and, consequently, a current in the direction of the external arrows. These currents, existing in all the molecular groups, are in fact those which are assumed to exist in Ampère's theory (p. 769): in unmagnetised iron, they run in all directions, and the effect of magnetisation is to reduce them to parallelism. Now, these currents cannot pass between the molecules composing the group unless these molecules are sufficiently close together; and, accordingly, it is found that magnetic bodies are, generally speaking, those whose atoms are most closely packed; in other words, those which have the smallest atomic volumes (p. 773). Moreover, heat, which increases the distance between the atoms, diminishes the magnetic power of a body, and may even destroy it altogether. Diamagnetic bodies, on the contrary, having, generally speaking, a large atomic volume,—that is to say, their atoms being very wide apart,—these atoms cannot discharge their opposite electricities one to another, but are in the state of the isolated atom (*fig.* 728). If, however, these independently polarised atoms are brought near an electric current, or the system of currents constituting a magnet, the atoms are brought, by the polarised molecules of the current, into such a position that the contrary poles of the two systems are brought face to face, as in the formation of induced currents (*fig.* 447, vol. ii. p. 454). Consequently, these atoms will place themselves, in their own group, in the same manner as those in *fig.* 729; and if the action is sufficiently powerful, the polarity of the atoms of the molecular group will be increased by their mutual influence, to such an extent, that discharges will take place between them, producing a current in the opposite direction to that of the magnet, in consequence of which the body will be repelled from the magnet. According to this theory, then, the chief difference between magnetic and diamagnetic bodies consists in this—that in the former the currents pre-exist round the molecular groups, and merely require to be brought to parallelism by magnetisation; whereas in the latter, they are brought into

Fig. 728.

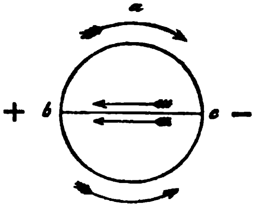
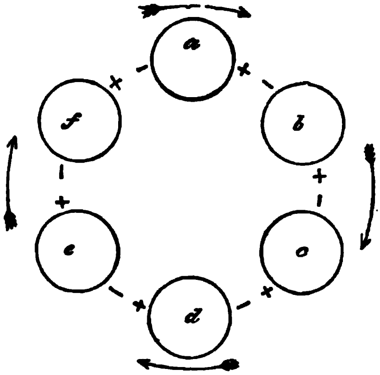


Fig. 729.



existence only under the influence of powerful currents, capable of bringing the atoms into the necessary arrangement.

There are, however, considerable difficulties in the reception of this theory. In the first place, the diamagnetic powers of bodies are by no means proportional to their atomic volumes. Potassium and sodium, which have much greater atomic volumes than bismuth, are slightly magnetic; whereas zinc and copper, whose atomic volumes are very small, are slightly diamagnetic. With regard to these two latter metals, De la Rive observes that they are very good conductors, and, therefore, that the recomposition of the opposite electricities may take place along the surface of each, in spite of their close proximity: and in support of this explanation he remarks, that on combining copper with chlorine and oxygen, which diminish its conductivity, it becomes magnetic. But this mode of explanation will not account for the magnetism of potassium and sodium, which are intermediate in conductivity between iron and copper. Moreover, it is difficult to see how, according to this theory, the diamagnetism of a body should be increased by compression. On the whole, it must be admitted that we are still very far from a satisfactory theory of diamagnetism.

MAGNETISM, TERRESTRIAL. The magnetic action of the earth has been spoken of in a general way in the preceding article: we shall here examine it more particularly. A magnetic needle suspended by its centre of gravity in such a manner that it can move freely in all directions, and placed beyond the influence of other magnets and masses of iron, places itself: 1. At a particular angle with the geographical meridian of the place: this is called the declination.—2. At a particular angle to the horizon, called the inclination or dip of the needle.

1. *Declination*—also called the *Variation of the Compass.*—The angle which the magnetic needle makes with the north and south line, or with the geographical meridian, is most conveniently observed with a needle whose movements are restricted to a horizontal plane; as by supporting it on a steel point by an agate cap (*fig.* 718), or on a stirrup of paper or copper suspended by a thread of unspun silk. When a needle thus suspended is carried to different parts of the earth's surface, its direction is continually changing. In certain parts of the world, it points exactly north and south; in all others, its position of equilibrium is more or less inclined to the geographical meridian of the place. A vertical plane passing through its position of equilibrium is called the magnetic meridian of the place.

The declination varies in direction and in amount both with place and with time. It is always spoken of with reference to the position of the north pole of the needle. Thus, when we say that the declination at London is at present to the west, we mean that the north pole of the needle points west of the geographical north.

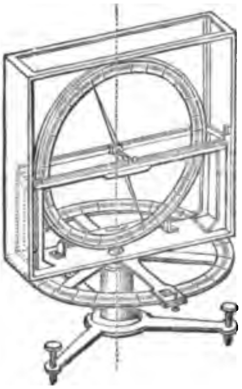
The points of the earth's surface at which the needle points due north and south are situated on certain lines, called *lines of no declination*. One of these lines, whose direction does not deviate much from that of a great circle of the globe, may be traced from a certain point north-west of Hudson's Bay, across Canada, into the Atlantic Ocean, cutting the extreme east point of South America, near Cape St. Roche, whence it passes across the South Atlantic Ocean, and meets the meridian of London near the 60th degree of south latitude. Another line of no declination passes across the Southern Ocean at about 120° east longitude, traverses the west of Australia in a nearly northerly direction, then passes westwards, forming a large loop enclosing the islands of the Indian Archipelago and the two peninsulas of India, whence it passes northwards along the west of Japan, and enters Siberia, where it has not been further traced. Another branch, which is perhaps a continuation of that which traverses the Indian Ocean, passes northwards across the White Sea. There are, therefore, two systems of lines of no declination, which probably join one another in the polar regions, so as to form a single curve passing round the globe.

Between the American line on the west and the Asiatic lines on the east—that is to say, over nearly the whole of the Atlantic Ocean and the Old World—the declination is to the west; over the rest of the earth's surface it is to the east; and it diminishes on both sides as we approach these lines. In London, at the present time (1864), the declination is 20° 45′ W.

Inclination or *Dip.*—Suppose a bar of unmagnetised steel to be suspended at its centre of gravity by a thread of unspun silk: it will come to rest in the horizontal position. But if it be magnetised, it will not only place itself in the magnetic meridian, but will take up an inclined position, the north pole in these latitudes pointing downwards. The amount of the inclination or dip of the needle is best observed by means of a long needle supported by its centre of gravity on a horizontal axis (*fig.* 730), so that its movements are confined to a vertical plane. A *dipping-needle* thus mounted is represented in *fig.* 730. The horizontal circle serves to place the plane of the needle's motion in the magnetic meridian, and the vertical circle to measure the dip.

As the needle always tends to place itself in the magnetic meridian, it is clear that if the vertical plane to which its movements are confined is placed at right angles to the magnetic meridian, the needle will stand vertically, this being the only position in which it can place itself in the magnetic meridian. If this position be determined and marked on the horizontal circle, the vertical circle may be placed in the magnetic meridian by moving it round 90° therefrom. The angle of inclination may then be directly observed.

Fig. 730.



The dip, like the declination, is of different amount in different localities. There are two points, one in each hemisphere, at which the dipping-needle stands exactly vertical; these are called the magnetic poles of the earth; and about midway between them is a line called the magnetic equator, or line of no dip, at which it stands horizontally. The magnetic equator is a somewhat sinuous line, not differing much from a great circle inclined to the geographical equator at an angle of 12°, and cutting it in two points near the longitudes 10° E. and 170° W., reckoned from the meridian of Paris. At all points between this line and the north magnetic pole, the north pole of the needle is directed downwards, the contrary being the case in the other magnetic hemisphere. The dip goes on increasing from the magnetic equator towards each pole: in London at the present time it is 68° 15′, reckoning from the horizontal plane.

On comparing the positions assumed by the needle at different parts of the earth's surface, it is easily seen that they may be accounted for by regarding the earth as a great magnet, having its poles at the points where the dipping needle stands vertically, and its median line coinciding with the magnetic equator. The northern terrestrial magnetic pole, which corresponds with the south pole of an ordinary magnet, is situated on the continent of North America, to the north-west of Hudson's Bay, and, according to the observations of Capt. J. C. Ross, made in 1830, in latitude 70° 5′ 17″ N, and longitude 96° 43′ W. from Greenwich (*Arago's Meteorological Essays, translated by Sabine*, p. 366). The position of the southern magnetic pole has been approximately fixed by the observations of the same navigator, in latitude 73° S. and longitude 130 E. The line of no declination passes through these two points, and the lines of equal declination converge towards them. From observations made at different points in England and the south of Scotland, between March 1858, and October 1860, Sabine deduces 68° 59′·2 as the dip at the mean epoch, 1st January, 1860, at a point whose latitude and longitude were the means of those of the stations included in the survey, namely latitude 52° 20′, longitude 1° 41′ W. from Greenwich. The minimum dip was observed at St. Leonard's (latitude 50° 51′, longitude 0° 33′ E.), where it was 67° 44′·5; and the maximum 71° 29′·5, at Jordan Hill, near Glasgow (latitude 55° 52′, longitude 4° 19′ W.), the direction of the *isoclinal lines*, or lines of equal dip, being from N. 71° 22′ E. to S. 71° 22′ W. (Rep. Brit. Assoc., 1861, p. 250).

That the earth really acts like a magnet, is further shown by the magnetisation of masses of iron placed in or near the line of the dip. In our latitude, where the line of dip does not differ greatly from the vertical, bars of iron standing constantly in the vertical directions, such as railings, lightning-conductors, &c., become magnetised with their north poles downwards, just as they would be if placed above the south pole of a steel magnet.

The magnetisation of the masses of iron in a ship by the earth's action, causes a considerable deviation of the compass-needle from its normal position; and as the direction of the magnetisation thus induced is constantly changing as the ship changes its latitude, it is evident that serious irregularities in the indications of the compass may thence result: in short, there are several instances of shipwreck on record which have been clearly traced to this cause. This source of irregularity may, however, be corrected by fixing a disc of iron, called a *compensator*, in such a position with regard to the compass, that its action shall be equal and opposite to that of the whole mass of iron in the ship: the needle will then be free to take up its normal position under the influence of the earth's magnetism. It is, however, found better in practice to place the compensator in such a position that it shall produce an action equal to that of the iron in the ship, and *in the same direction*, so that, when placed in position, it will double the deviation produced by the iron in the ship: the amount of this deviation will thus be ascertained, and may be allowed for. This great service to navigation is the invention of Mr. **Barlow**, of Woolwich.

The magnetic power of the native black oxide of iron is, doubtless, also due to the inductive action of the earth, and the very different powers exhibited by different specimens of the ore may, in part at least, be attributed to the different position of the veins with regard to the line of the magnetic dip.

3. *Intensity of the Earth's Magnetic force.*—The magnetic force of the earth, like that of an ordinary magnet, is of different intensity in different parts. The relative intensities at different places are measured by counting the number of oscillations made in a given time by a magnetic needle: for these vibrations are subject to the same laws as those of a pendulum, being isochronous when small, and the squares of the numbers of oscillations in a given time being proportional to the force which tends to bring the needle back to its position of equilibrium.

The observations may be made either with the dipping or the horizontal needle. When a dipping-needle is disturbed from its normal position of equilibrium, it is urged back to that position by the whole force of the earth's magnetism: so that, if the intensities of the terrestrial magnetic forces at any two places are devoted by F, F', and the corresponding number of oscillations made in a given time by n, n', we have, for the relation between the two forces,

$$F : F' = n^2 : n'^2.$$

The horizontal needle, on the other hand, is urged back to its normal position by only a portion of the terrestrial force, which becomes less as the magnetic latitude is greater. For the total force F acting on the needle in the line of the dip, may be resolved into two others, one vertical, which is destroyed by the suspension, the other, f, horizontal, which is that which is effective in moving the needle; and if i be the dip at the place of observation, this horizontal force f is equal to $F \cos i$. Hence, for any two places at which the total intensities are F, F', the angles of dip i, i', and the numbers of oscillations n, n', we have the relation,

$$\frac{n^2}{n'^2} = \frac{f}{f'} = \frac{F \cos i}{F' \cos i'}.$$

Therefore,

$$\frac{F}{F'} = \frac{n^2 \cos i'}{n'^2 \cos i}.$$

At the magnetic equator, $i = o$, $\cos i = 1$, and therefore $f = F$; at the magnetic poles, $i = 90°$, and therefore $f = 0$: in fact, at these points, the horizontal needle takes up all positions indifferently; and near the poles, the force which directs it is very small, so that its indications cannot be depended upon. But, excepting in these high magnetic latitudes, the results obtained with the horizontal needle are more trustworthy than those obtained with the dipping-needle, on account of errors affecting the latter, from want of perfect horizontality in the axis, the friction on the supports, &c.; whereas the horizontal needle is easily suspended by a thread of unspun silk, which gives it almost perfect freedom of motion. [For full details on the construction of instruments for observations on terrestrial magnetism, see Becquerel, *Traité de l'Electricité et du Magnétisme*, Paris, 1840, tome vii. The atlas to that work contains large diagrams of these instruments, and maps representing the directions of the magnetic meridians and parallels on the surface of the globe. See also Daguin, *Traité de Physique*, tome iii. pp. 27, 55.]

The magnetic intensity increases with the latitude. Humboldt found a point of minimum intensity on the magnetic equator in Northern Peru. This value is generally taken as the unit to which the magnetic intensities at other parts of the globe are referred, as in the following table.

Locality.	Date.	Latitude.	Magnetic intensity	Locality.	Date.	Latitude.	Magnetic intensity.
St. Anthony .	1802	0° 0′	1·087	Brussels . .	1829	50° 52′N	1·374
Carthagena .	1801	10 25 N	1·294	Berlin . .	1829	52 51	1·366
New York .	1822	40 43	1·803?	Christiania .	1820	59 55	1·419
Naples . .	1805	40 50	1·274	Petersburg .	1828	59 66	1·410
Lyons . .	1805	45 46	1·333	Baffin's Bay .	1818	62 43	1·590
Paris . .	1800	48 52	1·348	Spitzbergen .	1823	79 40	1·567

Referred to the same unit, the magnetic intensity was 1·372 in London in 1827 (Sabine)

According to Sabine, the intensity at the north magnetic pole is 1·624; at the south magnetic pole, according to Sir James Ross, it is 2·052. The smallest intensity, 0·706, observed by A. Erman, is at 19° 59′ S. and 10·2′ E. (from Paris).

In later observations made by British observers, an absolute unit of intensity has been adopted, corresponding with a second of time, a foot of space, and a grain of mass.

The magnetic intensity on this scale at London is at present 10·29; that is to say, it is a force capable of generating in one second, in a mass of one grain, a velocity of 10·29 feet per second. The total force, expressed in absolute units, has been observed to vary at different parts of the earth's surface from about 6·4 to 15·8. (Sabine, *Admiralty Manual of Scientific Inquiry*; ed. 1859, p. 89.)

The mean amount of the total force in England, deduced by Sabine from the magnetic survey already referred to (p. 780), for 1st January 1860, is 10·332, the minimum, 10·225, having been observed at St. Leonard's, and the maximum, 10·626, at Fern Tower (lat. 56° 22; long. 3° 50′ W.). The direction of the *isodynamic lines*, or lines of equal intensity, in England, at the above date, was from N. 57° 35′·7 E. to S. 57° 35′·7 W.

The isodynamic lines differ considerably from the isoclinal lines, or lines of equal dip, but bear considerable resemblance to the isothermal lines; whence it appears probable that the magnetic intensity of the earth (like that of an ordinary magnet) is affected by heat. (For a chart of these lines, see Becquerel, *loc. cit.*) According to Gauss, there are in each hemisphere two points of maximum magnetic intensity coinciding with the points of greatest cold, but not with the magnetic poles determined by the dip and declination of the needle.

Variations of the Magnetic Elements.

The declination, dip, and intensity at any point of the earth's surface are subject to continual variations, both regular and irregular; and the regular variations are of two kinds: secular variations, of considerable amount, and extending over long periods of time; and periodic variations, of small amount, and running through their phases at short intervals.

Variations of the Declination.—1. *Secular.* The earliest exact observations of the magnetic declination were made at London in 1576, and at Paris in 1580. At London, in 1576, it was 11° 15′ to the east; from that time it diminished till 1657–1662, when it was nothing, the needle then pointing due north and south; it then became westerly, attaining its maximum of 24° 36′ in 1800. In 1831 it had diminished to 24° 0′, and it is now (in 1864) 20° 45′ W. At Paris it was 11° 30′ E. in 1580, 0 in 1663, attained its maximum of 22° 34′ W. in 1814, and had diminished to 20° 25′ W. in 1851. At the Cape of Good Hope, the declination in 1605 was 0° 30′ E., became nothing between 1605 and 1609, then westerly, attaining its maximum of 25° 40′ W. about 1791. In all cases the declination given for each year is the mean of those obtained for each day and for each month, so as to eliminate the diurnal and annual variations.

2. *Annual.*—The declination of the needle is subject to small annual variations, which were discovered by Cassini in 1780. At Paris and London, it is greatest about the vernal equinox, diminishes from that time to the summer solstice, and increases again during the nine following months. The annual variation does not exceed from 15′ to 18′. It is also different in amount at different epochs. At London, from 1818 to 1820, it was reduced almost to nothing; at which time, also, the secular variation was extremely slow, being near its maximum.

3. *Diurnal.*—The diurnal variations of the declination were discovered by Graham in 1722. In Europe, the north pole of the needle begins to move westward at sunrise, and continues moving in the same direction till an hour or two after noon; after which it returns and regains its original position at about 10 P.M., at which it remains all night. It appears, then, that the westerly declination is greatest during the warmest part of the day. The amplitude of these movements is very small, and differs at different times of the year, being sometimes from 20′ to 25′, at other times not exceeding 5′ or 6′. It also becomes less as we approach the magnetic equator: thus, in the island of Rawak it never exceeds 3′ or 4′.

The periodic variations of the declination are the result of the superposition of two distinct variations,—one depending on the horary position of the sun, the other on his distance from the equator, the latter constituting the annual variation.

Variations of the Dip.—The secular variations of the magnetic dip are of smaller amount than those of the declination. At Paris, in 1671, when the dip was first observed, it was 73° 0′, and has since been continually diminishing; in 1851 it was 66° 35′. In London also the dip has continually diminished since 1720 by about 2′·6 per annum. In August, 1821, it was 70° 2′·81; in May, 1838, it was 69° 17′·30; in August and September, 1854, it was 68° 31′·13; it is now 68° 15′.

The dip likewise exhibits annual and diurnal variations, being, according to Hansteen, about 15′ greater in summer than in winter, and 4′ or 5′ greater before noon than after.

Variations of the Intensity.—It is not yet distinctly ascertained whether the magnetic intensity of the earth exhibits secular variations: indeed, the settlement of the question is attended with very great difficulty, inasmuch as it requires that the needles used should preserve their magnetic power unaltered throughout the whole course of the observations—a condition scarcely possible to fulfil for any great length of time. Gauss has found, indeed, by a peculiar method of observation which is independent of the force of the needles used, that the magnetic intensity at Göttingen has not varied sensibly during several years; but the time over which these observations have extended is as yet too short to warrant any general conclusion on the subject. It is, however, scarcely possible that the declination and dip should change at any place without some corresponding variation in the intensity. By absolute measurements made monthly at Kew since April, 1857, it appears that the total force had increased at that place, up to March 1862, at the average rate of 0·00125 annually.

Periodic variations of intensity are more easily observed. In studying these, it is usual to observe separately the variations of the horizontal and vertical components of the magnetic force. The horizontal component exhibits an hourly variation, which is the resultant of two elementary variations—one diurnal, the other semi-diurnal. The amplitude of the semi-diurnal variation increases with the latitude, and is nothing at the equator. The phases through which it passes depend on the angular distance of the sun from the magnetic meridian. In mean latitudes, the curve which represents the variation of the horizontal component is similar to that of the diurnal variation of the declination, but six hours behind it. The semi-diurnal period is scarcely perceptible at St. Helena, but increases in distinctness at higher latitudes.

The variations of the vertical component of the intensity follow the same periods as those of the horizontal components.

Irregular Variations or Perturbations of the Magnetic Elements.—The magnetic needle, especially the declination-needle, frequently experiences accidental deviations, which deflect it more or less from its normal position for various intervals of time, sometimes for several hours. Some of these disturbances may be traced to known causes,—namely, the *aurora borealis*, earthquakes, and volcanic eruptions. But few observations have been made on the perturbations arising from the two latter causes, which, moreover, produce sensible effects at small distances only. The deviations arising from these irregular disturbances rarely exceed a fraction of a degree, and the needle returns to its primitive position as soon as the disturbing cause has ceased to act.

The coincidence of the aurora borealis with certain perturbations of the magnetic needle was discovered in 1710 by Celsius and Hiorter. During the occurrence of an aurora, the declination-needle is seen to deviate from its normal position, even in localities where the meteor itself is not visible; so that the inspection of the needle often serves to announce the presence of an aurora, no trace of which can be directly seen. In our latitude, the deviation does not exceed 20′; but it is greater in the Arctic regions, where, indeed, the phenomenon has been principally studied. The culminating point of the auroral arch is always situated in the magnetic meridian of the place, and the centre of the crown to which the streams of light converge is situated on the prolongation of the line of the dip. So long as the auroral arch is stationary, the needle remains nearly at rest; but as soon as the arch begins to throw out streamers, the needle oscillates, sometimes through several degrees. The effects are more decided in proportion to the brightness of the aurora. The dip and the intensity are likewise affected by the aurora as well as the declination.

The establishment of magnetic observatories, in which the motions of the needle are observed continuously, has led to the discovery of perturbations which cannot be attributed to any of the preceding causes. One of the most remarkable facts brought to light, by observing the movements of the powerful magnets with which these establishments are furnished, is that the magnetism of the earth is in a state of constant fluctuation, like the waves of the sea. Hence, in studying the diurnal, annual, and secular variations of the declination, &c., it is necessary to take the mean of a large number of observations, in order to eliminate the irregular disturbances and bring out the general laws.

Another very remarkable phenomenon is the simultaneous occurrence of magnetic perturbations in very distant countries. Thus, Sabine mentions a magnetic disturbance which was felt simultaneously at Toronto, the Cape, Prague, and Van Diemen's Land. This coincidence of magnetic perturbations is so exact, that it has been proposed to make use of them in determining the longitude of the place of observation. Humboldt and Oltmann, in 1806, observed some remarkable perturbations recurring at the same hours for several successive nights. These simultaneous perturbances have received the name of *magnetic storms*.

There are also local perturbations extending to small distances only. Humboldt mentions one which was observed in the Saxon mines, but was imperceptible at Berlin. Magnetic storms observed simultaneously from Sicily to Upsala, were imperceptible between Upsala and Altona.

MAGNETO-ELECTRICITY. The development of electricity by magnetic action. (See ELECTRICITY, ii. 451.)

MAGNETOMETER. This name is specially applied to certain instruments devised by Gauss for measuring the intensity of the earth's magnetic force. (See Becquerel, *Traité de l'Electricité et du Magnetisme*, tome vii., and Daguin, *Traité de Physique*, iii. 78.)

MAGNIUM. Davy's name for Magnesium: it is also adopted by Gmelin in his *Handbuch*.

MAGNOFERRITE. A compound of ferric oxide and magnesia, $2Mg^2O.3Fe^4O^3$ or $3Mg^2O.4Fe^4O^3$, occurring in octahedral crystals among the products of the eruption of Vesuvius in 1855. Specific gravity about 4·6. (Rammelsberg, Pogg. Ann. cvii. 457; Jahresber. 1859, p. 776.)

MAHOGANY. See *Ure's Dictionary of Arts, &c.* iii. 16.

MAIZE. *Zea Maïs.*—The composition of the grain of this plant and of its ash is given in the article CEREALS (i. 825, 827). See also ZEIN. On the germination of maize, see v. Planta (Jahresber. 1860, p. 523). On the growth of maize in aqueous solutions of its constituents, see Stohmann (*ibid.* 1861, p. 734).

MAJORANA. See MARJORAM.

MAKWAH BUTTER. Syn. with GALAM BUTTER (ii. 758).

MALACHITE. Native carbonate of copper. (See CARBONATES, i. 783.)

MALACOLITE, also called *Sahlite, Pyrgom, Fassaite.*—A variety of augite, consisting of silicate of calcium and magnesium, with more or less iron (ferrosum), a small portion of the bases being frequently also replaced by water.

MALACONE. A mineral having the form of zircon, and nearly related to it in composition. Hardness = 6·5. Specific gravity = 3·9 to 4·05. Brown and vitreous to subresinous; powder reddish brown or uncoloured.

Analyses.—*a.* From Hitteroë, Norway, by Scheerer (Pogg. Ann. lxii. 436).—*b.* From the Ilmengebirg, by Hermann (J. pr. Chem. liii. 323).—*c.* From Chanteloube, Haute Vienne, by Damour (*Rammelsberg's Mineralchemie*, p. 891):

	SiO^2	ZrO^2	Fe^4O^3	Mn^4O^3	Y^2O	Ca^2O	Mg^2O	H^2O		
a.	31·31	63·40	0·41	. .	0·34	0·39	0·11	3·03	=	98·99
b.	31·87	59·32	3·11	1·20	. .	. .	. .	4·00	=	99·50
c.	31·05	61·44	3·29	0·14	. .	0·08	. .	3·09	=	99·09

These analyses lead to the formula $3(ZrO^2.SiO^2).H^2O$ or $3\overset{\prime\prime\prime\prime}{Zr}SiO^4.H^2O$, which requires 32·60 per cent. SiO^2, 64·22 ZrO^2, and 3·18 water.

MALAMIC ACID. } See MALIC ACID, AMIDES OF.
MALAMIDE. }

MALAMYLIC ACID. Syn. with AMYL-MALIC ACID. (See MALIC ETHERS.)

MALANIL. Syn. with PHENYL-MALIMIDE.

MALANILIC ACID. Syn. with PHENYL-MALAMIC ACID.

MALANILIDE. Syn. with PHENYL-MALAMIDE.

MALEIC ACID. $C^4H^4O^4 = \left.\begin{matrix}C^4\overset{\prime\prime}{H}{}^2O^2\\H^2\end{matrix}\right\}O^2$. *Pyromalic acid. Pyrosorbic acid.* (Lassaigne, Ann. Ch. Phys. [2] xi. 93.—Pelouze, *ibid.* lvi. 72.—Liebig, Ann. Ch. Pharm. xi. 276.—Büchner, *ibid.* xlix. 57.—Kekulé, Ann. Ch. Pharm. Suppl. i. 129; ii. 85; Jahresber. 1861, p. 364; 1862, pp. 308, 319.—Gm. viii. 151.)—An acid isomeric with fumaric acid, and differing from malic acid ($C^4H^6O^5$) by 1 at. water. It is produced, together with fumaric acid, by the dry distillation of malic acid. It has not yet been found ready formed in any plant. Equisetic acid, obtained from *Equisetum fluviatile*, was for some time regarded, on the authority of Regnault, as identical with maleic acid; but Baup has shown that it is really identical with aconitic acid ($C^6H^6O^6$).

To prepare maleic acid, malic acid is heated in a capacious retort, of which it fills about a fourth, the distillation being pushed on rapidly. Water then passes over first; afterwards, white vapours of maleic acid, which condense in the water. As soon as the residue in the retort thickens, the fire must be withdrawn; the distillation then goes on of itself for some time, till a solid residue is left in the retort, consisting of fumaric acid. An additional quantity of maleic acid may be obtained by distilling this residue at a higher temperature; but the product is then coloured and difficult to purify. By evaporating the distillate at a gentle heat, the maleic acid is obtained in crystals.

Maleic acid crystallises in oblique, rhomboïdal prisms, generally having their summits modified with octahedral faces. It is colourless and inodorous; its taste, sour at first, soon excites a very unpleasant sensation of nausea. It is very soluble in water and in alcohol; dissolves also in ether. The aqueous solution reddens litmus strongly; when left to itself in an open vessel, it creeps up the sides and effloresces in forms like cauliflower heads.

The crystals melt at about 130°, and the liquid acid begins to boil at about 160°, being then resolved into water and maleic anhydride, $C^4H^2O^3$. If the acid, instead of being rapidly heated to 160°, be boiled in a very long and narrow tube, so that the water which escapes is obliged to fall back upon it, the maleic acid is converted into the isomeric body fumaric acid. The same transformation takes place on heating the acid in a tube sealed at both ends.

Maleic acid is also converted into fumaric acid by heating it with concentrated *hydriodic* or *hydrobromic acid*, or by boiling for some time with dilute *nitric acid.* When hydriodic acid is used, the fumaric acid is subsequently converted into succinic acid.

Maleic acid in contact with water and *sodium-amalgam* takes up hydrogen, and is converted into succinic acid:

$$\begin{array}{cccc} \underset{\substack{\text{Maleic}\\\text{acid.}}}{C^4H^4O^4} & + \ H^2 & = & \underset{\substack{\text{Succinic}\\\text{acid.}}}{C^4H^6O^4} \end{array}$$

The same transformation takes place when maleate of calcium is fermented in contact with cheese. (Dessaignes.)

In contact with water and *bromine*, maleic acid is converted into dibromosuccinic acid, $C^4H^4Br^2O^4$, and another more soluble acid of the same composition, called isodibromosuccinic acid. (Kekulé.)

MALEATES.—Maleic acid is dibasic, forming *acid salts*, $C^4H^3MO^4$, and *neutral salts*, $C^4H^2M^2O^4$. The maleates bear considerable resemblance to the fumarates, with which they are isomeric; but they may be distinguished by the difference of solubility between fumaric and maleic acid: solutions of the maleates are not precipitated by other acids, whereas on adding a mineral acid to the solution of a fumarate (sufficiently concentrated and not warm) a precipitate of fumaric acid is formed.

Maleates of Ammonium.—*a.* The *neutral salt* is obtained as a crystalline jelly by saturating the aqueous solution of the acid with ammonia, and evaporating over lime *in vacuo.* Absolute alcohol added to the concentrated aqueous solution throws down the salt in the form of a white crystalline powder, which may be dried by repeated washing with alcohol, and pressing between paper, but, when exposed to the air, quickly becomes glutinous and deliquescent (Büchner). This salt does not precipitate a solution of sesquichloride of iron, a character which distinguishes it from the corresponding salt of aconitic acid.

β. The *acid salt* is obtained by exactly neutralising a known quantity of the aqueous acid with ammonia, then adding an equal quantity of the acid, and evaporating to the crystallising point at a gentle heat. It forms crystalline laminæ, which are permanent in the air, redden litmus, and give off nothing at 100°: their solution evolves ammonia when boiled; it is very easily soluble in water, but not in alcohol.

Maleates of Barium. *a. Neutral salt.* $C^4H^2Ba^2O^4.2H^2O$.—1. Maleic acid forms with baryta-water a pulverulent precipitate, which disappears on the addition of a small quantity of cold water, but reappears after a while in shining scales (Lassaigne). According to Pelouze, the precipitate is converted into the crystalline scales, even without addition of water. On adding a saturated solution of baryta-water to the concentrated aqueous acid, the precipitate redissolves at first in the excess of acid; even when sufficient baryta-water has been added to neutralise the acid, the precipitate is but small: but, after a few minutes, the whole solidifies to a tremulous gelatinous mass, resembling hydrate of aluminium, which, after being pressed, dries up to small crystalline laminæ. These crystals are obtained still more distinct on evaporating the aqueous solution (Regnault).—2. The salt is also obtained by adding carbonate of barium to the hot aqueous acid, as long as effervescence continues, then filtering hot, and leaving the solution to crystallise (Büchner).—3. The concentrated acid added to acetate of barium throws down a white crystallo-granular, neutral salt. Part of the salt, however, remains dissolved in the acetic acid which is set free, and may be precipitated by ammonia: this portion is also crystallo-granular, and has the same composition (Büchner). The salt crystallises from its aqueous solution on cooling, in small shining needles united in stellate groups; and the solution, when evaporated at a temperature below its boiling point, becomes covered with a crystalline crust (Büchner). The crystals, after drying in the air, lose 5·62 per cent. (1 at.) water at 100° (Büchner), and 7·3 per cent. at 150° (Regnault). They dissolve sparingly in cold water (in 9 pts. water at 20°, according to Regnault), with tolerable facility in boiling water, easily in aqueous maleic or acetic acid, easily also in excess of baryta-water.

β. Acid salt, $C^4H^3BaO^4.\frac{5}{2}H^2O$.—Obtained by saturating the aqueous acid with the neutral salt; or by saturating a known quantity of the boiling aqueous acid with carbonate of barium, and adding another equal quantity of acid to the hot filtrate. The resulting solution yields, after rather strong concentration, indistinct crystals, which redden litmus, give off the whole of their water of crystallisation (19·67 per cent.) at 100°, and dissolve in water, but not in alcohol. (Büchner.)

Maleates of Calcium.—*a.* The *neutral salt*, $C^4H^2Ca^2O^4.H^2O$, is obtained, according to Büchner, in small needles very soluble in water, but insoluble in alcohol, by saturating the boiling aqueous acid with carbonate of calcium and concentrating the filtrate at a gentle heat. According to Pelouze, a solution of maleate of potassium mixed with concentrated aqueous chloride of calcium remains clear, but after a few days deposits needles which are but sparingly soluble in water. By saturating the boiling acid with carbonate of calcium and evaporating the filtrate at a gentle heat, small needles are obtained united in saline crusts; they do not give off any water at 100°; dissolve readily in water, but not in alcohol (Büchner). This salt, when fermented with casein, is converted into succinate of calcium. (Dessaignes.)

β. The *acid salt*, $2C^4H^3CaO^4.5H^2O$, is formed by dissolving the neutral salt in a quantity of the aqueous acid equal to that which it already contains, and concentrating the solution somewhat strongly. It forms long rhombic prisms, which are permanent in the air, redden litmus, give off 24·1 per cent. ($\frac{5}{2}$ at.) of water at 100°, and dissolve readily in water, but not in alcohol. Oxalic acid added to the solution, throws down the lime. (Büchner.)

Maleate of Copper, $C^4H^2Cu^2O^4$.—1. On boiling carbonate of copper in the aqueous acid, the filtrate is found to contain in solution but a small quantity of salt, which crystallises out on evaporation; if the residue on the filter be freed from the carbonate of copper still adhering to it, by means of dilute acetic acid, which dissolves but a small quantity of the maleate, the latter remains in the form of crystals, which may be washed with cold water.—2. When a concentrated solution of acetate of copper is mixed with an equivalent quantity of maleic acid, and evaporated at a gentle heat, acetic acid goes off, and maleate of copper crystallises out; the crystals must be washed with cold water. The light blue crystals are but sparingly soluble in water, even at a boiling heat, but dissolve readily in aqueous ammonia. (Büchner.)

Maleate of Cuprammonium.—The dark blue solution of maleate of copper in ammonia may be evaporated, even near its boiling point, without loss of ammonia, and alcohol added to the concentrated solution precipitates the compound in the form of a neutral, azure-blue, crystalline powder, which gives off ammonia when heated with potash, and dissolves readily in water, but not in alcohol. (Büchner.)

Maleate of Iron (*ferricum*).—Neither maleic acid nor maleate of potassium precipitates ferric acetate; neither is ferric chloride precipitated by maleate of ammonium. A boiling solution of maleic acid dissolves a small quantity of ferric hydrate, forming a brownish solution which yields a red-brown syrup on evaporation.

Maleate of Lead, $C^4H^2Pb^2O^4.3H^2O$.—1. Free maleic acid forms a precipitate with neutral acetate of lead (Lassaigne), but not with the nitrate (Braconnot); if the solution is dilute, the white precipitate changes in a few minutes into shining micaceous laminæ; but if the solution is concentrated, and the acetate of lead in excess, the mixture solidifies to a tremulous mass, which changes slowly—or quickly on the addition of water—into crystalline laminæ, which with difficulty give off their 16·5 per cent. (3 at.) water (Pelouze).—2. Maleate of potassium added to nitrate of lead, throws down white flakes; these soon change to a translucent pasty mass, and then, when washed upon a filter, diminish considerably in volume, and are converted into small pearly needles (Lassaigne). The salt dissolves in nitric, but not in acetic acid. (Braconnot.)

Maleates of Magnesium. *a. Neutral salt*, $C^4H^2Mg^2O^4$ (at 100°).—The aqueous acid saturated at the boiling heat with carbonate of magnesium, yields a liquor which leaves on evaporation a tumefied spongy mass perfectly soluble in water. The concentrated solution of the salt yields with alcohol a bulky precipitate, which is not hygrometric, but gives off 27·36 per cent. water at 100°: it is very soluble in water and in dilute alcohol.

β. Acid salt, $C^4H^3MgO^4.3H^2O$.—By cooling a solution of 1 at. of the neutral salt, and 1 at. maleic acid in hot water, small transparent and colourless rhombic crystals are obtained, which redden litmus strongly, grate between the teeth, taste like Epsom salts, and dissolve readily in water, but are insoluble in alcohol. At 100°, they give off 34·95 per cent. water.

Maleate of Nickel, $C^4H^2Ni^2O^4.H^2O$.—By boiling the acqueous acid with carbonate of nickel, and evaporating the dark green, slightly acid filtrate, a gummy liquid is obtained, and ultimately apple-green crystals and crystalline crusts, insoluble in alcohol, but readily soluble in water. (Büchner.)

Maleates of Potassium. *a.* The *neutral salt*, $C^4H^2K^2O^4$ (at 100°), is obtained by saturating the acid with carbonate of potassium, and evaporating, in radiate crystals which are soft like wax, very soluble in water, but insoluble in alcohol. On adding alcohol to the concentrated aqueous solution, this salt is precipitated as a granulo-crystalline powder.

β. Acid salt, $2C^4H^3KO^4.H^2O$.—On saturating the acid with carbonate of potassium, adding an equal quantity of maleic acid, and cooling the solution, after sufficient concentration, this salt is obtained in small crystals very soluble in water; the solution reddens litmus. The salt is insoluble in alcohol. It does not give off any water at 100°.

On adding maleic acid to a concentrated solution of the neutral potassic salt, no precipitate is formed immediately, but the acid salt is deposited after some time. (Büchner.)

Maleates of Silver. α. Neutral, $C^4H^2Ag^2O^4$.—The acid gives no precipitate with nitrate of silver, but maleate of potassium or ammonium throws down a white precipitate (Lassaigne, Braconnot). The white precipitate obtained with an alkaline maleate changes in a few hours to tolerably large, transparent and colourless crystals, having an adamantine lustre; after drying, it detonates slightly on the application of a gentle heat. (Liebig.)

β. Acid salt, $C^4H^3AgO^4$ (at 100°).—Obtained in fine colourless needles by mixing a solution of maleic acid with nitrate of silver, and evaporating at a gentle heat.

Maleates of Sodium. α. Neutral, $C^4H^2Na^2O^4$.—The aqueous acid saturated with carbonate of sodium and evaporated, yields a magma of needles on cooling. The salt is precipitated from its aqueous solution by alcohol, as a crystalline powder. It is not deliquescent.

β. The *acid salt*, $C^4H^3NaO^4.3H^2O$, obtained like the acid potassium-salt, forms rhomboïdal prisms, sparingly soluble in cold, more soluble in boiling water, insoluble in alcohol. The solution has an acid reaction. The crystals contain 28·3 per cent. crystallisation-water, which they give off at 100°.

Sodio-potassic maleate, $C^4H^2KNaO^4.H^2O$.—On neutralising an aqueous solution of maleate of sodium with carbonate of potassium, then evaporating and cooling the syrup, a few small crystals are obtained, floating in a gelatinous mother-liquid. On precipitating the concentrated aqueous solution with absolute alcohol, and setting the crystalline magma aside in contact with absolute alcohol, there is finally obtained a white, easily deliquescent, crystalline powder, which gives off 9·13 per cent. (2 at.) water at 100°, and contains 25·55 per cent. potash, and 17·64 per cent. soda. (Büchner.)

Neither the ammonio-potassic nor the ammonio-sodic salt has yet been obtained.

Maleates of Strontium.—*α.* The *neutral salt*, $C^4H^2Sr^2O^4.5H^2O$, forms silky needles.—*β.* The *acid salt*, $C^4H^3SrO^4.4H^2O$, obtained like the corresponding barium-salt, crystallises in rectangular prisms, which are limpid, and acid to litmus-paper. The salt is soluble in water, but insoluble in alcohol. It gives off the whole of its water (31·4 per cent.) at 100°. (Büchner.)

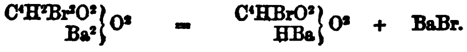
Maleate of Zinc, $C^4H^2Zn^2O^4.2H^2O$.—On boiling the aqueous acid with carbonate of zinc, and evaporating the filtrate at a gentle heat, gelatinous flocks are deposited, which become completely crystalline on standing. The solution when heated, deposits the salt in crystalline crusts. The crystals do not lose anything at 100°; they are very soluble in water, but insoluble in alcohol. (Büchner.)

Substitution-derivatives of Maleic Acid.

Maleic acid does not yield substitution-products by the direct action of chlorine or bromine; but compounds have been obtained by indirect processes, having the composition of these substitution-products, and analogous to maleic acid in their properties.

Bromomaleic acids. These compounds are produced by the decomposition of the brominated derivatives of succinic acid.

Monobromomaleic acid, $C^4H^3BrO^4$.—Of this acid there are four modifications. One of them, usually called bromomaleic acid, is obtained, as an acid barium-salt, by boiling an aqueous solution of dibromosuccinate of barium:



$$\left.\begin{matrix} C^4H^2Br^2O^2 \\ Ba^2 \end{matrix}\right\}O^2 \quad = \quad \left.\begin{matrix} C^4HBrO^2 \\ HBa \end{matrix}\right\}O^2 \quad + \quad BaBr.$$

Bromomaleic acid, obtained from this barium-salt in the usual way, crystallises readily in large nodules, formed of prismatic crystals. It melts between 125° and 126°, and is resolved, at about 150°, into water and bromomaleic anhydride, an oily liquid, which, after repeated rectification, boils at about 212°, and in contact with water is slowly reconverted into the acid.

Bromomaleic acid is converted by sodium-amalgam into succinic acid. It does not, like bromomalic acid, yield tartaric acid when boiled with lime. When heated to 100°

with water and *bromine*, it yields a crystallisable, deliquescent acid, which appears to be dibromotartaric acid:

$$C^4H^3BrO^4 + 2Br^2 + 2H^2O = C^4H^4Br^2O^6 + 3HBr.$$

Bromomaleic acid is dibasic. Its salts usually form nodules of indistinct crystals. The *silver-salt*, $C^4HBrAg^2O^4$, separates, on mixing bromomaleate of ammonium with nitrate of silver, as a white amorphous precipitate, which may be crystallised without decomposition from boiling water. (Kekulé.)

Isobromomaleic acid. This acid, isomeric with the preceding, is produced by heating isodibromosuccinic acid to 180°, or by boiling and evaporating its aqueous solution:

$$C^4H^4Br^2O^4 = C^4H^3BrO^4 + HBr;$$

also by boiling isodibromosuccinic anhydride with water.

Isobromomaleic acid, is very much like bromomaleic acid, but melts at a higher temperature, viz. 160°. Its *silver-salt* is easily decomposed by boiling with water.

Isobromomaleic anhydride, $C^4HBrO^2.O$, is obtained, with evolution of hydrobromic acid, on heating isodibromosuccinic anhydride to 180°. It is crystallisable.

Two other acids having the composition of bromomaleic acid, viz. *meta-* and *para-bromomaleic acid*, are found, together with dibromosuccinic acid, in the most soluble portion of the secondary products resulting from the action of bromine on succinic acid. Both are crystallisable and very soluble in water. The former melts at 126°—127°; the latter at 172°. Their silver-salts are more stable than that of isobromomaleic acid.

Dibromomaleic acid, $\left.\begin{matrix}C^4Br^2O^2\\H^2\end{matrix}\right\}O^2$.—This acid is produced, in small quantity, together with dibromosuccinic acid, and the two last-mentioned modifications of monobromomaleic acid, by the action of bromine on succinic acid. It is found in the last mother-liquors, and may be obtained therefrom by distillation and slow evaporation of the distillate. It is probably a product of the decomposition of previously formed tribromosuccinic acid.

Dibromomaleic acid crystallises in nodular groups of large needles. It is extremely soluble, and volatilises with the aqueous vapours. Melts at 112°. Its *lead-* and *silver-salts* are crystalline precipitates, which detonate when heated; the silver-salt, also, by percussion. (Kekulé, *Lehrbuch d. org. Chemie*, ii. 315.—Ann. Ch. Pharm. cxxxi. 1.)

Chloromaleic acid. $\left.\begin{matrix}C^4HClO^2\\H^2\end{matrix}\right\}O^2$.—Obtained by the action of pentachloride of phosphorus on tartaric acid. When 1 pt. of tartaric acid is heated with 5 or 6 pts. of the pentachloride, large quantities of hydrochloric acid are evolved, together with oxychloride of phosphorus, which must be removed by prolonged heating to 120° in a current of air. The residue consists of oily *chloride of chloromaleyl*, $C^4HClO^2.Cl^2$, which is resolved by water into hydrochloric and chloromaleic acids.

The reaction may be explained as follows:—The first product of the action of pentachloride of phosphorus on tartaric acid is the tetrachloride of the radicle of that acid:

$$\underset{\text{Tartaric acid.}}{\left.\begin{matrix}C^4H^2O^2\\H^4\end{matrix}\right\}O^4} + 4PCl^5 = \underset{\text{Tetrachloride of tartryl.}}{C^4H^2O^2.Cl^4} + 4POCl^3 + 4HCl,$$

and this tetrachloride, which is identical with dichloride of dichlorosuccinyl, is resolved by heat (in a manner analogous to the decomposition of isodibromosuccinic acid, already mentioned) into hydrochloric acid and dichloride of monochloromaleyl:

$$\underset{\text{Dichloride of dichlorosuccinyl.}}{C^4H^2Cl^2O^2.Cl^2} = \underset{\text{Dichloride of chloromaleyl.}}{C^4HClO^2.Cl^2} + HCl.$$

Chloromaleic acid forms white microscopic needles, soluble in water and fusible by heat. It is dibasic. The *lead-* and *silver-salts* are crystalline precipitates. (Perkin and Duppa, Ann. Ch. Pharm. cxv. 105.)

Isomaleic acid, $C^4H^4O^4$.

Isomalic acid (p. 794), treated with pentachloride of phosphorus, yields a chloride, which, when in contact with water, is converted into this acid, isomeric with maleic acid.

Isomaleic acid is crystallisable, less soluble in water than maleic acid, more soluble than fumaric acid. The *neutral potassium-salt* forms deliquescent crystals. The *lead-salt* is an amorphous precipitate. The *silver-salt* is very soluble in water, and its solution, when boiled, deposits metallic silver. (Kämmerer, J. pr. Chem. lxxxviii. 321; Jahresber. 1863, p. 379.)

MALEIC ANHYDRIDE. $C^4H^2O^3 = C^4H^2O^2.O$. (Pelouze, Ann. Ch. Pharm.

xi. 263.—Kekulé, *ibid.* Suppl. ii. 87.)—This compound is obtained by rapidly distilling maleic acid, and rectifying the product several times, the first portion of the distillate being each time rejected. It is a white crystalline mass, which melts at 57°, and boils at 196°. In contact with water it is converted into maleic acid.

Maleic anhydride unites directly with bromine, producing a substance which has the composition of dibromosuccinic anhydride, $C^4H^2Br^2O^2.O$, is converted by water into isodibromosuccinic acid, and is resolved at 180° into hydrobromic acid and isobromomaleic anhydride. (Kekulé.)

MALIC ACID. $C^4H^6O^5 = \left.\begin{matrix}(C^4H^3O^2)''\\H^3\end{matrix}\right\}O^3$. (Gm. x. 205.—Gerh. i. 787.)—This acid was discovered by Scheele in 1785, but its composition was first correctly determined by Liebig (Ann. Ch. Pharm. xxvi. 166). It is very widely diffused in the vegetable kingdom, and is contained in plants, sometimes in the free state, sometimes in the form of a potassium-, calcium-, or magnesium-salt. It is found in abundance, together with citric acid, in unripe apples, in the fruits of the barberry, sloe, elder, and mountain-ash, and in gooseberries, cherries, bilberries, strawberries, raspberries, and many other acid fruits. It is likewise found in the roots of marsh-mallow, angelica, aristolochia, bryony, liquorice, primrose, and madder; in carrots and potatoes; in the leaves and stems of aconite, belladonna, hemp, celandine, holy thistle, lettuce, tobacco, poppy, rue, sage, house-leek, tansy, thyme, valerian and melilot; in the flowers of chamomile, elder, and mullein; in pine-apples and grapes; in the seeds of carraway, cumin, parsley, anise, flax, and pepper; in asafœtida, opopanax, myrrh, &c.

Malic acid, as it exists in plants, exerts a rotatory action on polarised light. An acid having exactly the same composition and properties, including the rotatory power, is produced, according to Piria (Ann. Ch. Phys. [3] xxii. 160), by the action of nitrous acid on asparagin or on active aspartic acid; but, by acting with nitrous acid upon inactive aspartic acid (produced by the metamorphosis of fumarimide), Pasteur has obtained a modification of malic acid destitute of rotatory power (Ann. Ch. Phys. [3] xxxiv. 46).

Malic acid is found, according to Berzelius, among the residues of the preparation of nitrous ether. Debus (Ann. Ch. Pharm. c. 1) could not detect malic acid in these residues, but found instead, glyoxylic acid.

Preparation.—From the berries of the Mountain-ash. These likewise contain small quantities of tartaric and citric acid, especially while very unripe. (Liebig.)

The juice of mountain-ash berries, not quite ripe, after being pressed, boiled up and filtered, is partly neutralised with carbonate of potassium, leaving, however, a sufficient excess of acid to redden litmus pretty strongly; then precipitated by nitrate of lead (or with neutral acetate of lead, if carbonate of potassium is not used); set aside for a few days, till the curdy precipitate is completely converted into small needles; these crystals freed from the admixed mucous or flocculent compound of lead-oxide and colouring matter (which is particularly abundant when acetate of lead is used) by careful elutriation with cold water; and, lastly, well washed with water.—*a.* The needles are boiled with a quantity of dilute sulphuric acid not sufficient to decompose the whole of them, as long as any granular deposit continues to subside; the uniform pulpy mass mixed with aqueous sulphide of barium, till a filtered sample is found to contain baryta; the liquid filtered (the sulphide of lead then acting as a decolorising agent); the colourless filtrate boiled with excess of carbonate of barium; the liquid again filtered (tartrate and citrate of barium remaining on the filter); the baryta precipitated from the filtrate by careful addition of dilute sulphuric acid; and the filtrate, which should show no turbidity, either with sulphuric acid or with chloride of barium, evaporated to the crystallising point. If the filtrate should become turbid on addition of sulphuric acid, it must be evaporated down, the residue exhausted with alcohol; the liquid filtered from the remaining malate of barium; and again evaporated.—*b.* Or the needles of impure malate of lead are boiled with a slight excess of dilute sulphuric acid; the filtrate divided into two equal portions; one portion exactly neutralised with ammonia; the other portion then added; and the reddish liquid evaporated and cooled; it then yields nearly colourless crystals of acid malate of ammonia, which may be rendered quite colourless by recrystallisation. These crystals are then precipitated by acetate of lead, and the precipitate, after thorough washing, is decomposed by sulphydric or sulphuric acid. (Liebig.)

By similar processes, malic acid may be obtained from house-leek, from cherries or barberries, from the berries of *Rhus coriaria*, from the stems of rhubarb, from apples, and from tobacco.

Properties.—The aqueous solution of malic acid concentrated to a syrup, and then left to evaporate in a warm place, yields groups of colourless shining needles or prisms of 4 or 6 faces. They melt at 83° C. (Pelouze), at 100° (Pasteur), and do not suffer any loss of weight at 120°. They are odourless, have a sour taste, and deliquesce in the air. Malic acid is soluble in alcohol.

The aqueous solution of active malic acid rotates the plane of polarisation of a luminous ray to the left: $[\alpha] = -5°$. Some of its salts possess dextro-rotatory, others lævo-rotatory power. The presence of acids, whether mineral or organic, increases the tendency to lævo-rotation. (Pasteur.)

Decompositions.—1. The acid heated for some hours to between 175° and 180° in a retort placed in the oil-bath, is resolved, without any evolution of gas or carbonisation, into water, maleic acid, which passes over in the liquid form with the water, and crystallises soon afterwards, and about an equal quantity of fumaric acid (ii. 741), part of which distils over, while the rest remains in the retort in the form of a crystalline mass. If the malic acid be suddenly heated to 200°, and kept for some time at that temperature, a comparatively large quantity of maleic acid is obtained; but at 150°, the malic acid is very slowly, but almost completely, resolved into water and fumaric acid. The first product of the decomposition perhaps consists entirely of maleic acid, which, however, if the heat be not quickly raised to the point of volatilisation, is converted into fumaric acid. (Pelouze.)

If a strong fire be made to act immediately on the malic acid, it swells up, turns brown, and yields, together with maleic and fumaric acids, large quantities of carbonic oxide and carbonic anhydride, empyreumatic oil, and charcoal, which must be regarded as decomposition-products of the maleic and fumaric, not of the malic acid. (Lassaigne).—2. In the open fire, the acid burns with the odour of burnt sugar.—3. The acid in combination with potash is decomposed by *bromine*, with formation of bromoform (Cahours, Ann. Chim. Phys. [3] xix. 507).—4. *Nitric acid* easily converts it into oxalic acid, with evolution of carbonic anhydride.

5. By the action of *reducing agents* it is converted into succinic acid. The reduction takes place readily on heating it with concentrated *hydriodic acid* to 130° (Schmitt, Ann. Ch. Pharm. cxiv. 106); also when malate of calcium is fermented in contact with yeast. (Piria, *ibid.* lxx. 102; Liebig, *ibid.* 104, and 363.)

6. By slow oxidation in the cold with *acid chromate of potassium*, it is converted into malonic acid (Dessaignes, Ann. Ch. Pharm. cvii. 251):

$$\underset{\substack{\text{Malic}\\\text{acid.}}}{C^4H^6O^5} + O^2 = \underset{\substack{\text{Malonic}\\\text{acid.}}}{C^3H^4O^4} + H^2O + CO^2.$$

When heated with chromate of potassium and sulphuric acid, it gives off all its carbon as carbonic anhydride (Döbereiner). Boiled in dilute aqueous solution with *peroxide of manganese*, it yields a distillate containing aldehyde (Liebig, Ann. Ch. Pharm. cxiii. 14).

7. Malic acid gently heated with excess of *potassic hydrate*, is resolved into oxalic and acetic acids:

$$C^4H^4K^2O^5 + KHO = C^2H^3KO^2 + C^2K^2O^4 + H^2.$$

When malate of calcium (1 pt.) is heated with *pentachloride of phosphorus* (4 pts.), chloride of fumaryl passes over (Perkin and Duppa (*ibid.* cxii. 24). When malic acid (1 at.) is heated with the pentachloride (2 at.) till it begins to turn brown, and the product is decomposed with water, fumaric acid is obtained. (Liès-Bodart, *ibid.* c. 327.)

MALATES.—Malic acid, though most probably triatomic, as shown by the constitution of its amides (p. 796), contains only 2 at. hydrogen replaceable by metals. It may therefore be conveniently represented by the formula $\left.\begin{matrix} H \\ (C^4H^3O^2)''' \\ H^2 \end{matrix}\right\}O^3$ (similar to that of glycollic acid, which is diatomic but monobasic), and the neutral and acid malates by the formulæ $\left.\begin{matrix} H \\ C^4H^3O^2 \\ M^2 \end{matrix}\right\}O^3$, and $\left.\begin{matrix} H \\ C^4H^3O^2 \\ H.M \end{matrix}\right\}O^3$. Malic acid has a great tendency to form acid salts.

The active and inactive modifications of malic acid yield respectively active and inactive salts. The former sometimes exhibit hemihedral modifications; the latter are always holohedral.

The malates heated to 200° give off water, and are converted into fumarates:

$$C^4H^4M^2O^5 = C^4H^2M^2O^4 + H^2O.$$

Nearly all malates are soluble in water. A solution of the acid or of a malate is not precipitated by *lime-water* or *chloride of calcium*, either in the cold or on heating; but on the addition of alcohol, a white precipitate of calcic malate separates. Neutral malate of calcium is also precipitated by long boiling of a solution of malic acid, nearly neutralised with milk of lime. With *acetate of lead*, malic acid forms a white precipitate soluble in excess of malic acid and in ammonia: this precipitate when heated in its mother-liquid, melts to a semifluid, transparent mass. Malates are not blackened by heating with *fuming sulphuric acid;* this reaction distinguishes malic from citric and tartaric acids.

Malates of Aluminium.—The *neutral salt* is a transparent gum, which reddens litmus slightly, is permanent in the air, and dissolves readily in water, forming a solution which is not precipitated by potash or ammonia. There is also a *basic salt* sparingly soluble in water.

Malates of Ammonium.—*a.* The neutral salt is very soluble and uncrystallisable.

β. The *acid salt*, $C^4H^5(NH^4)O^5$, is prepared by treating malate of lead with dilute sulphuric acid, taking care to avoid an excess of acid, filtering, dividing the liquid into two parts, saturating one with ammonia, then adding the other, and evaporating to a syrup. The salt prepared with optically active malic acid crystallises in fine transparent prisms, belonging to the trimetric system, with well-defined and strongly reflecting faces. Ordinary combination, $\infty P . \infty\breve{P}\infty . \frac{1}{2}\breve{P}\infty$, sometimes with hemihedral facets $\frac{P}{2}$. Inclination of the faces, $\infty P : \infty P = 71° 36'$; $\frac{1}{2}\breve{P}\infty : \frac{1}{2}\breve{P}\infty$, in the plane of the brachydiagonal and vertical axis $= 137° 35'$; $\breve{P}\infty : \breve{P}\infty$ in the same plane $= 103° 36'$. Cleavage easy, perpendicular to the faces ∞P. The salt, when crystallised from pure water, or from water acidulated with nitric acid, is never hemihedral; but the crystals acquire that character when melted till they begin to decompose, and then recrystallised. It would appear, therefore, that the action of heat gives rise to the formation of small quantities of products which induce the development of hemihedral faces. Specific gravity of the crystals = 1·55 (that of water at 12·5° = 1). The crystals dissolve in 3·11 pts. of water at 15·7°. The solution deflects the plane of polarisation to the left: rotatory power for 100 millimetres: $[\alpha] = -6°$ or $-7°$. If the salt is dissolved in nitric acid, it becomes dextro-rotatory: $[\alpha] = +5·6°$. By dry distillation, it gives off water, and leaves an insoluble residue of fumarimide (ii. 746). Ammonia escapes, however, together with the water, and the residue contains fumaric and maleic acids, together with malic acid both active and inactive.

The acid ammonium-salt of inactive malic acid forms two kinds of crystals.—(*a*) The solution when evaporated first yields crystals having the same composition as the active ammonium-salt, and the same form, with exception of the hemihedral faces, which are absent.—(*b*) The mother-liquor separated from these crystals deposits, after a while, large, hard, transparent crystals containing 2 at. water more than the salt *a*, and belonging to the monoclinic system. Ordinary combination, $\infty P . [\infty Pn] . [P\infty]$. Inclination of faces, $\infty P : \infty P$ in the plane of the clinodiagonal and principal axis $= 124° 19'$; $[\infty Pn] : \infty P = 149° 33'$; $[P\infty] : [P\infty]$ in the plane of the clinodiagonal and principal axis $= 127° 20'$; $[P\infty] : \infty P = 85° 22'$ and $119° 22'$. Angle of the inclined axes = 110° 56'. No hemihedral faces. Inactive acid malate of ammonium is decomposed by heat in the same manner as the active salt.

Active acid malate of ammonium unites in atomic proportion with acid dextrotartrate of ammonium; the inactive salt does not.

Malates of Antimony.—The neutral salt has not been obtained.

Malate of Antimony and Ammonium is obtained, according to Pasteur, by boiling a solution of acid malate of ammonium with antimonic oxide. The liquid left to evaporate yields the double salt in large crystals, having the hemihedral faces very fully developed. The solution is dextro-rotatory; for 100 millimetres: $[\alpha] = +115·47°$.

Malate of Antimony and Potassium is obtained in the crystalline state by saturating acid malate of potassium with antimonic oxide. Neither of these double salts has been analysed.

Malates of Barium. *a. Neutral salt*, $C^4H^4Ba^2O^5.2H^2O$?—It is difficult to saturate malic acid with carbonate of barium, so completely that the liquid shall no longer redden litmus-paper. The solution evaporated in a vacuum deposits transparent plates neutral to test paper, and giving off 10·6 per cent., water at 220°. The solution when boiled deposits white crusts of the anhydrous salt, having no appearance of crystallisation; they are absolutely insoluble in water whether cold or boiling, but dissolve rapidly on adding a trace of nitric acid; the solution thus formed is not precipitated by ammonia.

β. Acid-salt.—Uncrystallisable and more soluble than the preceding.

Malates of Calcium. *a. Neutral salt*, $C^4H^4Ca^2O^5$.—1. Malic acid does not become turbid on addition of excess of lime-water (Braconnot, Ann. Ch. Phys. [2] li. 331; Lassaigne); not even in concentrated solutions and on the application of heat,—a character by which malic is distinguished from citric acid (H. Rose, Pogg. Ann. xxxi. 210; Winckler). The acid neutralised with lime-water yields on evaporation in vacuo (an acid mother-liquid remaining) large, thin, shining laminæ, which dissolve readily in water, and after drying in vacuo at ordinary temperatures, give off all their water = 17 per cent. (2 at.) at 180°, and about half of it at 100°. Their aqueous solution, when left to evaporate in the air, again yields laminæ, but when heated to the boiling point, deposits a white, granular, nearly insoluble salt with 1 at. water. Hence the laminæ, in parting with half their water, likewise lose their solubility. (Richardson and Menzdorf, Ann. Ch. Pharm. xxvi. 135.)

2. Dilute malic acid agitated in the cold with excess of carbonate of calcium, remains strongly acid; but the filtrate, when boiled, coagulates to a pulp composed of granules of the monohydrated neutral-salt, which is nearly insoluble in water and in aqueous malic acid (Richardson and Menzdorf). From the solution thus obtained, the neutral salt separates in four-sided prisms, which grate between the teeth, dissolve in 83 pts. of cold and a somewhat smaller quantity of hot water (Lassaigne); or as a granular powder of anhydrous salt, which is nearly insoluble both in hot and in cold water. (Hagen, Ann. Ch. Pharm. xxxviii. 257.)

3. The same granular powder is thrown down from the aqueous solution of the acid salt by several hours' boiling. (Hagen.)

4. A mixture of aqueous chloride of calcium and neutral malate of sodium deposits, after a while, the neutral malate of calcium, in transparent crystalline grains. This salt scarcely froths up in the fire; it is completely decomposed by the soluble alkaline carbonates. It dissolves in 147 pts. of cold water, forming a solution which tastes somewhat like nitre, and in at most 65 pts. of boiling water, from which it does not separate on cooling. (Braconnot.)

5. The solution of acid malate of calcium neutralised with a soluble alkaline carbonate, yields, by evaporation at a gentle heat, hard shining crystals of the neutral salt, which contain 3 at. water, give off 1 at. water at 100°, assuming the appearance of porcelain, and are completely dehydrated at 150°. (Hagen.)

6. The granular salt, left to itself in the moist state for two days, takes up water, and is converted, under circumstances not yet determined, into rough, translucent, globular crystals, which, after drying in the air, whereby they are rendered opaque, give off 22·49 per cent. (3 at.) water at 200°. (Dessaignes and Cathaurd, J. Pharm. [3] xiii. 243.)

Neutral malate of calcium is easily obtained in the crystalline state by dissolving the acid malate in ammonia, and leaving the solution to evaporate. If the solution is dilute, an abundant crop of crystals is obtained in 24 hours; but if the salt is dissolved in hydrochloric acid, and ammonia then added in excess, it takes a considerable time to crystallise.

The crystalline form of this salt is hemihedral, and it produces dextro-rotation, whether dissolved in water or in hydrochloric acid. (Pasteur.)

Neutral malate of calcium, kept for some months under a shallow layer of water in a vessel covered with paper, is converted into succinate (Dessaignes). During the winter, crystallised hydrated carbonate of calcium and a mucous organisation are likewise produced; but in the summer months, the sole product consists of needles of succinate of calcium, which gradually rise above the diminishing malate of calcium, while a small quantity of gas is given off. (Dessaignes, Compt. rend. xxviii. 16.)

When a mixture of 4 pts. of malate of calcium, 24 pts. of water, and 1 pt. of yeast (or a smaller quantity of putrefying cheese or fibrin) is set aside in a warm place, a tolerably brisk evolution of pure carbonic anhydride takes place, the muddy calcium-salt begins in the course of three days to become granular and heavy, and after the evolution of gas is terminated, appears under the microscope to consist of transparent needles united in stellate groups, and composed of succinate and carbonate of calcium. The supernatant liquid contains acetate of calcium.

If too much yeast or cheese is used, or if the mixture becomes too hot, hydrogen gas is evolved as well as carbonic anhydride, and possibly in equal volume; and in that case there is obtained but little succinic and acetic, but a large quantity of butyric acid, and a colourless, volatile oil, smelling of apples, which may be obtained by distilling the liquid; this oil dissolves readily in water, and may be separated therefrom by chloride of calcium or carbonate of potassium: it, however, dissolves a larger quantity of chloride of calcium in the dry state. For the fermentation in which succinic and acetic acid are produced, and pure carbonic anhydride is evolved, the equation is:

$$3C^4H^6O^5 = 2C^4H^6O^4 + C^2H^4O^2 + 2CO^2 + H^2O.$$

For the fermentation, when hydrogen is evolved:

$$2C^4H^6O^5 = C^4H^8O^2 + 4CO^2 + H^2$$

or, if the evolution of hydrogen is consequent on the decomposition of succinic acid:

$$3C^4H^6O^4 = 2C^4H^8O^2 + 4CO^2 + H^2.$$

Part of the carbonic acid remains with the lime. (Liebig, Ann. Ch. Pharm. lxx. 104, and 363.)

According to E. J. Kohl (Ann. Ch. Pharm. lxxviii. 252), malate of calcium fermented with putrefying casein gives off nothing but carbonic anhydride, and yields principally lactate of calcium, with small quantities of succinate, acetate, and carbonate. W. Baer (Arch. Pharm. [2] lxix. 147) obtained a similar result with the juice of mountain-ash berries, neutralised with carbonate of calcium, mixed with beer-yeast, and left to stand at ordinary temperatures. Winckler (Jahrb. pr. Pharm. xxii. 300) found a large quantity of lactic acid in the acid residue of cider, and supposes it to have been formed by fermentation of the malate of calcium contained in the juice of the apples. Rebling (Arch. Pharm. [2] lxvii. 300) observed that, in the fermentation of malate of calcium, valerianic acid is formed as well as succinic and butyric acids.

When a solution of *inactive malic acid* is neutralised with lime-water, no turbidity is produced; but on addition of alcohol, the neutral calcium-salt is deposited in white amorphous flakes. On boiling the neutralised aqueous solution, a granulo-crystalline precipitate is formed, having the composition $C^4H^4Ca^2O^5$, and but sparingly soluble in water, either hot or cold. When a solution of acid malate of ammonium, containing the inactive acid is mixed with a soluble calcium-salt and excess of ammonia, no precipitate is formed at first, but after 24 hours, transparent crystals united in nodules are formed, containing $2C^4H^4Ca^2O^5.5$ aq. (Pasteur.)

β. Acid salt, $C^4H^5CaO^5.4H^2O$. — This salt may be prepared from the stems of *Geranium zonale* (Braconnot). Also from the berries of *Rhus glabrum* or *copallinum*, by exhausting them with hot water, evaporating the infusion, decolorising it with animal charcoal previously purified with hydrochloric acid, evaporating the filtrate further, setting it aside to crystallise, and purifying the resulting crystals, if necessary, by recrystallisation (Rogers, Sill. Am. J. xxvii. 294). Tobacco also contains it in large quantity. The solution of the neutral salt in warm dilute nitric acid, deposits the acid salt in crystals on cooling. (Hagen.)

The crystals of the salt prepared with the active acid belong to the trimetric system. Ordinary combination, $\infty P . \infty \breve{P}n . \infty \breve{P}\infty . \breve{P}\infty . m\breve{P}\infty$. Inclination of the faces, $\infty P : \infty P = 93° 26'$; $\infty P : \infty \breve{P}n = 162° 14'$; $\infty \breve{P}\infty : \infty \breve{P} = 133° 17'$; $\infty \breve{P}\infty : \breve{P}\infty = 136° 33'$; $\breve{P}\infty : m\breve{P}\infty = 163° 30'$. Cleavage easy parallel to $\infty P\infty$. When crystallised from pure water, it does not exhibit hemihedral faces; but when crystallised from nitric acid, all the crystals have four faces $\frac{mP}{2}$, and for a certain concentration of the acid, these facets become so much developed as nearly to obliterate the principal faces of the crystal. The crystals dissolve in 50 pts. of cold water, and in a much smaller quantity of boiling water: they are insoluble in absolute alcohol. They give off 22·37 per cent. (nearly 3 at.) water at 100°, and are completely dehydrated at 180°.

The inactive salt resembles the preceding in every respect, excepting that it has no hemihedral faces.

According to Braconnot, acid malate of calcium saturated with alkaline carbonates yields double salts, viz. *ammonio-*, *potassio-*, and *sodio-calcic malates;* but they have not been analysed.

Malates of Copper.—*a.* The *neutral salt*, $C^4H^4Cu^2O^5.H^2O$, is a gummy mass of a fine green colour, and very soluble in water.

β. The *acid salt*, $C^4H^5CuO^4.H^2O$, is obtained in fine blue crystals, by saturating the cold aqueous acid with cupric hydrate and evaporating at 40°.

γ. A *basic salt*, $2C^4H^4Cu^2O^5.Cu^2O.4H^2O$, is obtained, as a green insoluble powder, by boiling malic acid in excess with cupric carbonate. The carbonate treated in the cold with excess of malic acid dissolves in considerable quantity, and the solution, when boiled, immediately deposits the salt just mentioned; but if evaporated in a vacuum between 40° and 50°, it deposits dark green crystals containing the same proportion of malate and oxide of copper with 6 at. water.

A mixture of cupric sulphate and malate of ammonium deposits by spontaneous evaporation, first crystals of cupric sulphate, then green acicular crystals unalterable in the air, of a *double salt*, consisting of cupric malate and sulphate of ammonium. (H. Schulze, Arch. Pharm. [2] lvii. 273.)

Malate of Iron (*ferricum*).—Both the neutral and acid salts are brown, gummy, permanent in the air, very soluble in water and in alcohol. A solution of a ferric salt containing malic acid is not precipitated by alkalis.

Malates of Lead.—*a.* The *neutral salt*, $C^4H^2Pb^2O^4.3H^2O$, is obtained by precipitating neutral acetate of lead with a solution of calcic or potassic malate; it is a white curdy precipitate, which, when left for some hours in a solution of the acetate, is converted into four-sided needles grouped around a common centre. This salt melts in boiling water to a transparent pitchy mass; it is very slightly soluble in cold, more soluble in boiling water; a strong aqueous solution deposits it in shining needles. It dissolves very easily in nitric acid; acetic acid and malic acid do not dissolve it more freely than pure water. Acetate of lead also dissolves the malate, and deposits it by slow evaporation in silky needles.

According to R. Otto (Ann. Ch. Pharm. cxxviii. 175), a neutral malate of lead having, after drying at 100°, the composition $C^4H^4Pb^2O^5.H^2O$, is obtained by dropping a partly neutralised solution of malic acid into an excess of boiling aqueous solution of basic acetate of lead, boiling for several hours with de-aërated water, and washing by decantation.

Both the active and inactive malates of lead melt with equal facility in boiling water; the only difference observed between the two modifications is that the inactive salt takes a longer time than the active salt to become crystalline, the latter, which is amorphous at the time of precipitation, being converted into needle-shaped crystals in a few hours, whereas the inactive salt may remain amorphous for several days. This character may serve to distinguish between the two salts, when only small quantities of them are at hand. Both salts melt immediately on being immersed in boiling water, but a portion dissolves and is precipitated when the liquid cools and is left at rest; the active malate is then deposited after 24 hours in shining prisms grouped in tufts; the inactive salt, on the contrary, is deposited in the amorphous state, and covers uniformly the sides of the vessel; but after a few days, this amorphous precipitate disappears, and is replaced by needle-shaped crystals, also grouped in tufts, and exactly resembling those of the active malate. (Pasteur.)

Malate of lead in the amorphous state easily parts with the whole of its combined water (14 per cent. = 3 at.) when dried over sulphuric acid. If the salt is crystallised, the water is retained with greater force, and it must be heated to about 150° to dehydrate it.

Neutral malate of lead, which melts easily when thrown into boiling water, does not melt in the hot air chamber, either at 100° or at a higher temperature. It even retains its crystalline aspect up to 170°, in spite of the loss of its water of crystallisation, and only then begins to assume a dull woolly aspect. When heated to 220°, it gives off more water, and is converted into fumarate of lead.

β. A *basic salt*, $Pb^2O.2C^4H^4Pb^2O^5$, is obtained by digesting the neutral salt with ammonia, or by pouring acetate of lead into the solution of a malate mixed with ammonia, or, according to Otto (*loc. cit.*), by dropping a perfectly neutralised solution of malic acid into excess of a boiling solution of basic acetate of lead. It never becomes crystalline, and does not melt in boiling water, but if acetic acid be added, it melts, with considerable diminution of volume, being then evidently converted into the neutral salt.

Basic malate of lead dissolves in acetate of lead, like the neutral salt, and the solution, if somewhat concentrated, is precipitated by ammonia. It is nearly insoluble in water, either cold or boiling; but sufficiently soluble to blue red litmus paper, when a few moist fragments are placed upon it.

Malates of Lithium.—Both the neutral and acid salt are uncrystallisable.

Malates of Magnesium.—α. *Neutral salt*, $C^4H^4Mg^2O^5.5H^2O$. A dilute solution of malic acid boiled with magnesia yields a liquid which, when evaporated to a pellicle, deposits after some time, rhomboïdal prisms of this salt, containing 5 at. water, four of which are given off at 100°. Alcohol added to the concentrated solution precipitates it in anhydrous flocks, which become pasty by heat.

β. The *acid salt*, $C^4H^5MgO^5.2H^2O$, is obtained in flattened prisms, by half saturating malic acid with carbonate of magnesium, and evaporating to crystallisation. It gives off half its water at 100°, and melts at a higher temperature.

Malates of Manganese.—α. The *neutral salt*, which is uncrystallisable and very soluble, is obtained by saturating the acid with carbonate of magnesium. The *acid salt* is precipitated as a white powder, on adding malic acid to a solution of the preceding salt. It dissolves in 41 pts. of cold water, and is deposited from boiling water in transparent rose-coloured crystals.

Malates of Mercury.—These salts have not been analysed. When malic acid is digested with *mercurous oxide*, a crystalline powder is formed. The same salt is obtained on mixing malate of potassium with a dilute solution of mercurous nitrate. It is decomposed by boiling with water.

When *mercuric oxide* is boiled with a strong solution of malic acid, the filtered liquid deposits small crystals of an acid salt soluble in water; with excess of mercuric oxide, an insoluble yellow basic salt is formed. (Harff, Arch. Pharm. [3] v. 281.)

Malate of Potassium.—α. *Neutral.* Uncrystallisable, deliquescent, insoluble in strong alcohol (Braconnot).—β. *Acid.* Crystals, permanent in the air, soluble in water, insoluble in alcohol. (Donovan.)

Malate of Silver, $C^4H^4Ag^2O^5$.—Nitrate of silver forms, with a solution of neutral or acid malate of ammonium, a white granular precipitate, which becomes yellow when thoroughly dried. If heated after drying, it melts and decomposes, swelling up a little, emitting an empyreumatic odour, and leaving perfectly white metallic silver. The *acid* malate of silver has not been obtained.

Malates of Sodium.—The *neutral salt* is uncrystallisable. The *acid salt* is crystalline, permanent in the air, soluble in water, insoluble in alcohol.

Malates of Strontium. α. *Neutral salt*, $C^4H^4Sr^2O^5.H^2O$ (at 100°).—Malic acid is not rendered turbid by strontia-water; but, on evaporating the mixture, a crystalline mass is obtained, very soluble in water. When malic acid is digested with carbonate of strontium, a solution is obtained which slightly reddens turmeric, and deposits after concentration mammellated groups of crystals having the above composition.

β. An *acid salt* is precipitated in the crystalline state on adding malic acid to an aqueous solution of the neutral salt; it is but slightly soluble in cold water, more soluble in boiling water.

Malate of Thallium crystallises with difficulty; it is deliquescent, and melts below 100°. (Kuhlmann.)

Uranic Malate.—Yellow; sparingly soluble in water. (Richter.)

Malate of Yttrium.—1. When an aqueous solution of malic acid is poured upon carbonate of yttrium, part of the resulting salt dissolves, and is obtained by evaporation in small white nodules.—2. Neutral alkaline malates throw down from yttrium-salts—when the solutions of the two salts are concentrated and mixed in due proportion—a white, almost crystalline powder, which remains in white granules when its aqueous solution is evaporated.—The air-dried salt is $C^4H^4Y^2O^5.H^2O$. It does not give off its water at 110°, and is but slowly decomposed at higher temperatures. It dissolves in 74 pts. of water; its solution in aqueous malic acid deposits the neutral salt unchanged. It dissolves abundantly in aqueous malate of sodium, and does not crystallise on evaporation. (Berlin.)

Malates of Zinc. α. *Neutral salt*, $C^4H^4Zn^2O^5.3H^2O$.—When the aqueous acid is saturated with carbonate of zinc at a temperature below 30°, the filtrate deposits, after a while, small shining crystals which gradually but completely give off their 3 at. water at 100° (Hagen). When, on the other hand, the acid is saturated at a high temperature, and the solution filtered from a basic salt which separates on cooling, and further evaporated, crystals are deposited, containing indeed 3 at. water, but having a different form, and obstinately retaining about $\frac{3}{4}$ at. water at 100° (Hagen). They are short hard, strongly lustrous, four-sided prisms (square, according to Lassaigne), perpendicularly truncated, or bevelled with two faces; they redden litmus (Braconnot). They become opaque at 100°, giving off 10 p. c. of water, and at 120° swell up and crumble to a white powder, giving off at the same time 10 p. c. more water (Liebig). They dissolve in 55 pts. (67 pts. at 20°, according to Lassaigne) of cold, and 10 pts. of boiling water, from which the salt does not separate on cooling. (Braconnot.)

β. *Acid salt*, $C^4H^5ZnO^5.2H^2O$.—Obtained by supersaturating the salt α with the acid, and washing the resulting crystals with alcohol. It forms elongated square-based octahedrons, which swell up when heated, giving off 8·33 per cent. water, and are converted into a gum; they dissolve in 23 pts. of cold water. (Braconnot.)

γ. *Basic salt*, $Zn^2O.2C^4H^4Zn^2O^5.4H^2O$?—This salt remains, on dissolving the neutral salt in water, as a crystalline residue, containing 48·11 per cent. zinc-oxide (Braconnot). The solution obtained by continuous boiling of the aqueous acid with carbonate of zinc, solidifies on cooling to a tremulous jelly, which by prolonged boiling with water is converted into a sandy powder. This powder is not decomposed by water at 100°, but at 200° it gives off water, and is partially converted into fumarate of zinc. (Hagen.)

Bromomalic acid. $C^4H^5BrO^5$.—No substitution-products have yet been obtained from malic acid; but when an aqueous solution of dibromosuccinate of sodium is boiled, and then evaporated, a mass of crystals is obtained, having the composition of acid bromomalate of sodium, $C^4H^4BrNaO^5$. From this salt, other bromomalates may be formed by double decomposition; but the acid itself has not yet been obtained.

Acid bromomalate of sodium is distinguished from the bromomaleate (p. 787) and its isomers, by yielding tartrate of calcium when boiled with lime-water. (Kekulé, *Lehrbuch*, i. 185.)

Isomalic acid, $C^4H^6O^5$.

An acid, isomeric with malic acid, and perhaps identical with diglycollic acid (ii. 912), the silver-salt of which was deposited from a photographic silver-bath containing nitrate of silver and milk-sugar, which had been used for a long time for dipping papers soaked in succinic or citric acid. The free acid separated by sulphydric acid from the silver-salt, forms a crystalline mass, or by slow crystallisation, transparent, well-developed crystals resembling those of augite. The *acid ammonium-salt*, $C^4H^5(NH^4)O^5\ 2H^2O$, remains, on evaporating the neutralised acid with ammonia, as a radio-crystalline mass. The *neutral potassium-salt*, $C^4H^4K^2O^5.H^2O$, crystallises in monoclinic laminæ. The *lead-salt* is a white precipitate, perfectly insoluble in water, and not melting or baking together in boiling water. The *silver-salt*, $C^4H^4Ag^2O^5$, which is flocculent at first, is converted, when warmed with water, into microscopic six-sided tables, which do not decompose at 100°. This salt, treated with iodide of ethyl, yields the *neutral ethylic ether*, $C^4H^4(C^2H^5)^2O^5$, as a colourless liquid, gradually decomposed by water.

The isomalates, treated with pentachloride of phosphorus, yield a chloride isomeric with chloride of fumaryl, according to the equation:

$$C^4H^4M^2O^5 + 3PCl^5 = 2MCl + 2HCl + 3POCl^3 + C^4H^2O^2Cl^2.$$

This chloride is a liquid, which is partly decomposed by distillation, and, in contact with water, is resolved into hydrochloric acid and isomaleic acid, $C^4H^4O^4$ (p. 788). (Kämmerer, J. pr. Chem. lxxxviii. 321.)

MALIC ACID, AMIDES OF. When ammonia is passed into an alcoholic solution of ethylic malate, small crystals of malamide are gradually deposited:

$$\underset{\text{Malate of ethyl.}}{C^4H^4(C^2H^5)^2O^5} + 2NH^3 = \underset{\text{Malamide.}}{C^4H^8N^2O^3} + \underset{\text{Alcohol.}}{2C^2H^6O};$$

and when dry ethylic malate is saturated with ammonia-gas, the product soon solidifies to a crystalline mass of ethylic malamate or malamethane, $C^6H^{11}NO^4 = \left.\begin{matrix} H \\ (C^4H^3O^2)''' \\ C^2H^5.H^2 \end{matrix}\right\}\begin{matrix} O^2 \\ N \end{matrix}$, the decomposition being represented by the equation:

$$C^4H^4(C^2H^5)^2O^5 + NH^3 = C^6H^{11}NO^4 + C^2H^6O.$$

This latter compound, dissolved in alcohol and saturated with ammonia, likewise yields malamide.

Malamide crystallises, by slow evaporation, in well-defined crystals. It differs from the metameric compound asparagine (i. 421) by its crystalline form, by not containing any water of crystallisation, and by its property of easily taking up water, and being thereby converted into ammonia and malic acid. It differs also in optical rotatory power: $[\alpha] = -47{\cdot}5$. (Demondesir, Ann. Ch. Pharm. lxxx. 303.—Pasteur.)

Malamic acid, $C^4H^7NO^4$, which is metameric with aspartic acid (i. 422), has not been isolated.

If malic acid be regarded as triatomic and dibasic, and represented by the formula $\left.\begin{matrix} H \\ C^4H^3O^2 \\ H^2 \end{matrix}\right\} O^3$ (p. 790), in which two out of the three typic hydrogen-atoms are *saline*, that is, easily replaceable by metals, and the third, *alcoholic*, that is, most easily replaceable by acid-radicles (see ii. 915), the difference between malamic acid and malamide on the one hand, and aspartic acid and asparagine on the other, may be represented by formulæ analogous to those of glycollic monamide (the so-called glycollamide, ii. 908) and glycocine (ii. 902), thus:

$$\underset{\text{Malic acid.}}{\left.\begin{matrix} H \\ (C^4H^3O^2)''' \\ H^2 \end{matrix}\right\} O^3} \qquad \begin{matrix} \underset{\text{Aspartic acid.}}{\left.\begin{matrix} H^2 \\ (C^4H^3O^2)''' \\ H^3 \end{matrix}\right\}\begin{matrix} N \\ O^2 \end{matrix}} & \underset{\text{Asparagin.}}{\left.\begin{matrix} H^2 \\ (C^4H^3O^2)''' \\ H.H^2 \end{matrix}\right\}\begin{matrix} N \\ O \\ N \end{matrix}} \\ \underset{\text{Malamic acid.}}{\left.\begin{matrix} H \\ (C^4H^3O^2)''' \\ H.H^2 \end{matrix}\right\}\begin{matrix} O \\ N \\ O \end{matrix}} & \underset{\text{Malamide.}}{\left.\begin{matrix} H \\ (C^4H^3O^2)''' \\ H^2H^2 \end{matrix}\right\}\begin{matrix} O \\ N^2 \end{matrix}} \end{matrix}$$

Aspartic acid bears the same relation to malic acid that glycocine bears to glycollic acid. The saline or basic hydrogen of malic acid is still present in aspartic acid, but the alcoholic water-residue HO of the malic acid is replaced in aspartic acid by the ammonia-residue NH^2. Asparagine is the amide of aspartic acid. Hence it is that aspartic acid is not decomposed by boiling with alkalis (the ammonia-residue not being in the saline place), and that asparagine, when treated in the same way, gives off only half its nitrogen as ammonia, and is converted into aspartic acid. In malamic acid, on the other hand, the ammonia-residue occupies the saline place; and, consequently, when malamide, which is its amide, is boiled with alkalis, the decomposition does not stop at the formation of malamic acid, but goes on to the formation of malic acid and ammonia.

The neutral amide (triamide) of malic acid, $\left.\begin{matrix}H^2\\(C^4H^3O^2)'''\\H^2.H^2\end{matrix}\right\}N^3$, is not known.

Malamic acid and malamide may be derived from the acid and neutral malates of ammonium by elimination of 1 and 2 at. water respectively, and, by further abstraction of water, the other compounds in the following table may be conceived to be formed, though only one of them, viz. fumarimide (ii. 746), has actually been obtained:

$\left.\begin{matrix}H\\(C^4H^3O^2)'''\\H^4N\\H^4N\end{matrix}\right\}O^3$	$\left.\begin{matrix}H\\(C^4H^3O^2)'''\\H^2\\H^2\end{matrix}\right\}\begin{matrix}O\\N^2\end{matrix}$	$\left.\begin{matrix}H\\(C^4H^3O^2)'''\\H^2\end{matrix}\right\}N^2$	$\left.\begin{matrix}H\\(C^4H^3O)^{v}\end{matrix}\right\}N^2$
Neutral malate of ammonium.	Malamide.	(unknown.)	Nitrile (unknown).
$\left.\begin{matrix}H\\(C^4H^3O^2)'''\\H.H^4N\end{matrix}\right\}O^3$	$\left.\begin{matrix}H\\(C^4H^3O^2)'''\\H.H^2\end{matrix}\right\}\begin{matrix}O^2\\N\end{matrix}$	$\left.\begin{matrix}H\\(C^4H^3O^2)'''\\H\end{matrix}\right\}\begin{matrix}O\\N\end{matrix}$	$(C^4H^3O^2)'''.N$
Acid malate of ammonium.	Malamic acid.	Malimide (unknown).	Nitrile (Fumarimide).

Malic acid was formerly regarded as diatomic as well as dibasic, being represented by the formula $\left.\begin{matrix}(C^4H^4O^3)''\\H^2\end{matrix}\right\}O^2$, which agrees perfectly with the constitution of its salts. Moreover, the formulæ of malamic acid and malamide are easily derived from it; but then the so-called fumarimide cannot be supposed to contain the same radicle, but must actually be regarded as the imide of fumaric acid; thus:

$\left.\begin{matrix}H\\(C^4H^4O^3)''\\H\end{matrix}\right\}O^2$	$\left.\begin{matrix}(C^4H^4O^3)''\\H^2\\H^2\end{matrix}\right\}N^2$	$\left.\begin{matrix}H^2\\(C^4H^4O^3)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$	$\left.\begin{matrix}(C^4H^2O^2)\\H\end{matrix}\right\}N$
Malic acid.	Malamide and asparagin.	Malamic acid and aspartic acid.	Fumarimide.

But the formation of this compound by heating acid malate of ammonium to 160°—200°, and its conversion into inactive aspartic acid by boiling with strong hydrochloric acid, show that it is intimately related to malic acid, and, therefore, that the triatomic formula of malic acid, which renders it possible to express fumarimide by a formula containing the same radicle as the acid, must be regarded as preferable (Kekulé). Moreover the relation of malic acid to succinic and tartaric acids cannot be adequately expressed by a diatomic formula.

Substances closely resembling fumarimide or malonitrile, are likewise obtained, according to Dessaignes, by the action of heat on acid fumarate and acid maleate of ammonium.

MALIC ACID, PHENYLATED AMIDES OF. These compounds have been more completely studied than the primary amides of malic acid; three of them have been obtained by Arppe (Ann. Ch. Pharm. xcvi. 106), viz. diphenyl-malamide, phenyl-malimide, and phenyl-malamic acid.

Diphenyl-malamide. Malanilide. $C^{16}H^{16}N^2O^3 = \left\{\begin{matrix}H\\(C^4H^3O^2)'''\\(C^6H^5)^2.H\end{matrix}\right\}\begin{matrix}O\\N^2\end{matrix}$.—This compound is formed, together with phenyl-malimide, by melting malic acid with aniline:

$$\underset{\text{Aniline.}}{2C^6H^7N} + \underset{\text{Malic acid.}}{C^4H^6O^5} - 2H^2O = \underset{\text{Diphenyl-malamide.}}{C^{16}H^{16}N^2O^3}.$$

$$C^6H^7N + C^4H^6O^5 - 2H^2O = \underset{\text{Phenyl-malimide.}}{C^{10}H^9NO^3}$$

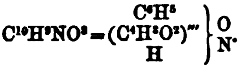
The product treated several times with boiling water, is resolved into a nearly colourless solution containing phenyl-malimide, and a strongly coloured residue consisting chiefly of diphenyl-malamide, which may be obtained pure and colourless by crystallisation from boiling alcohol, with the aid of animal charcoal.

It forms colourless scales having a faint lustre; melts, with partial decomposition, at 175°, and at a higher temperature volatilises for the most part unaltered. When set on fire it burns with a bright smoky flame.

It is nearly insoluble in *water*, and in dilute *hydrochloric acid*, *ammonia*, and *potash*. It dissolves also but sparingly in *alcohol* and *ether*. Strong *sulphuric acid* dissolves it with the aid of heat. *Nitric acid* dissolves it in the cold, forming a yellow solution.

When boiled with strong caustic *potash*, it dissolves and is for the most part decomposed, a fatty substance rising to the surface of the liquid. On addition of water, the semifluid portion is converted into a white insoluble powder, which may be completely freed from potash by washing with water. This powder dissolves with some difficulty in alcohol, and crystallises therefrom in small crystalline groups and needles. It may be heated, without visible alteration, to 225°; melts at a higher temperature; and if cautiously heated, yields a crystalline laminar sublimate, and leaves a small quantity of charcoal. This substance gives by analysis 64·17 per cent. carbon and 5·41 hydrogen: hence it appears to be *tartranilide*. (Arppe.)

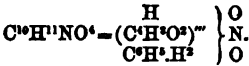
$$C^{16}H^{16}N^2O^4 = 2C^6H^7N + C^4H^6O^6 - 2H^2O;$$

Phenyl-malimide. Malanil.  $C^{10}H^9NO^3 = \left.\begin{matrix}C^6H^5\\(C^4H^3O^2)'''\\H\end{matrix}\right\}\begin{matrix}O\\N.\end{matrix}$ —Formed, together with the preceding compound, by melting a mixture of malic acid and aniline. When the fused mixture is kept in a state of gentle ebullition for about two hours, a brown syrup is obtained, which solidifies on cooling, and when boiled with water, yields a nearly colourless solution of phenyl-malimide, and a coloured residue containing diphenyl-malamide. The solution when evaporated yields phenyl-malimide in the form of a granular mass, still, however, mixed with diphenyl-malamide, from which it is purified by digestion in hot water, and filtration. The solution is then further purified by treatment with animal charcoal, and evaporated to the crystallising point.

From a hot concentrated aqueous solution, phenyl-malimide separates on cooling in delicate needles grouped together; also when its alcoholic solution is evaporated; sometimes, however, it forms nacreous laminæ, and from a very dilute aqueous solution it is deposited in very thin, iridescent, rectangular prisms. It melts at 170°, and when heated between two watch-glasses, forms a slight mealy sublimate. It dissolves very abundantly in *water*, *alcohol*, and *ether*.

Phenyl-malimide, boiled with aqueous *ammonia*, is converted into phenyl-malamate of ammonium.

It dissolves easily in the strongest *nitric acid*, forming a deep red solution from which water throws down a nearly colourless, indistinctly crystalline body, probably nitro-phenyl-malimide, accompanied by a resinous body which is very difficult to separate. The crystalline body dissolves easily in boiling water, and the solution on cooling yields fine needles. (Arppe.)

Phenyl-malamic acid. Malanilic acid.  $C^{10}H^{11}NO^4 = \left.\begin{matrix}H\\(C^4H^3O^2)'''\\C^6H^5.H^2\end{matrix}\right\}\begin{matrix}O\\N.\\O\end{matrix}$ —This acid is obtained in the form of an ammonium-salt by boiling phenyl-malimide with aqueous ammonia (*vid. sup.*). The solution of this salt forms with baryta a copious precipitate, which, when mixed with a small quantity of water, and decomposed, with the aid of heat, by an exactly equivalent quantity of sulphuric acid, yields phenyl-malamic acid; and from the solution, filtered while yet warm, the acid crystallises on cooling, and may be purified by recrystallisation from alcohol. The slightest excess of sulphuric acid used in the preparation converts the phenyl-malamic acid into phenyl-malimide; hence it is best to use rather less than the equivalent quantity.

The acid crystallises in white, faintly lustrous granules, composed of very minute needles, and scarcely attaining the size of a pin's head; melts at 145°; has a very sour taste, reddens litmus, and decomposes carbonates; dissolves readily in *water*, somewhat less in *alcohol*, and sparingly in *ether*. Its salts are also distinguished by their solubility in water.

The solution of the ammonium-salt remains clear when mixed with *lime-water*, but is slightly clouded by boiling with *potash*; with *acetate of lead*, it forms a white precipitate soluble in water; and with *sesquichloride of iron*, a precipitate of a fine yellow colour.

The *barium-salt* is very soluble in water, and crystallises in spherical nodules of a dazzling whiteness; it is insoluble in hydrochlorate of ammonia.

Phenyl-malamate of silver, $C^{10}H^{10}AgNO^4$, forms a white precipitate, which soon becomes coloured by exposure to light; it dissolves in water, and is deposited from the solution in shining cubes.

MALIC ETHERS. These compounds have not been much studied. According to Demondesir (Compt. rend. xxiii. 227), the malates of ethyl and methyl are produced by passing hydrochloric acid gas into a solution of malic acid in alcohol or wood-spirit. The neutral ethers cannot be distilled; they are obtained by neutralising the crude liquid with carbonate of sodium and agitating with common ether, which takes up the ethylic or methylic malate, and leaves it behind on evaporation. The compound ether thus obtained still contains water and alcohol or wood-spirit, which may be removed by evaporation in a vacuum.

The neutral malates of ethyl and methyl are liquids which are soluble in water, almost completely decomposed by distillation, being converted into the corresponding fumaric ethers, and are converted into malamide by ammonia. They possess optical rotatory power.

Ethyl- and Methyl-malic acids are always formed by the above process simultaneously with the neutral ethers. Their calcium-salts are soluble in alcohol.

Amyl-malic acid, $C^4H^5(C^5H^{11})O^5$, is obtained by prolonged heating of malic acid with amyl-alcohol to 120°. It forms a syrup which crystallises on cooling. (Breunlin.)

MALOÏLE. Syn. with Oil of Apples (i. 532; ii. 636).

MALONIC ACID. $C^3H^4O^4 = \left.\begin{matrix}(C^3H^2O^2)''\\ H^2\end{matrix}\right\}O^2$. An acid discovered by Dessaignes (Ann. Ch. Pharm. cvii. 251), who obtained it by slowly oxidising malic acid with a cold solution of chromate of potassium:

$$\underset{\text{Malic acid.}}{C^4H^6O^5} + O^3 = CO^2 + H^2O + \underset{\text{Malonic acid.}}{C^3H^4O^4}.$$

It is also produced, with evolution of ammonia, by the action of alkalis on cyanacetic acid, or better on cyanacetic ether:

$$\underset{\text{Cyanacetic acid.}}{C^2H^3(CN)O^2} + 2H^2O = NH^3 + \underset{\text{Malonic acid.}}{C^3H^4O^4}$$

$$\underset{\text{Cyanacetic ether.}}{C^2H^2(CN)(C^2H^5)O^2} + 3H^2O = NH^3 + \underset{\text{Alcohol.}}{C^2H^6O} + \underset{\text{Malonic acid.}}{C^3H^4O^4}$$

The solution obtained by boiling cyanacetic ether* with potash, forms with sulphate of copper, a green precipitate, which by decomposition with sulphydric acid, and evaporation of the filtrate, yields malonic acid. (Hugo Müller, Chem. Soc. J. xvii. 109.)

Malonic acid forms large rhombohedral crystals, having a laminar structure. It dissolves easily in *water* and *alcohol*, melts at 140°, and decomposes at 150° into carbonic anhydride and acetic acid.

The malonates have been but little examined. The *neutral potassium-* and *ammonium-salts* are deliquescent and crystallise with difficulty; the *acid salts* of the same bases crystallise readily. The *barium-* and *calcium-salts* are crystalline precipitates sparingly soluble in cold water. The *silver-salt* is insoluble and crystalline; the *lead-salt* is likewise insoluble.

An acid called nicotic acid, obtained by Barral (Compt. rend. xxi. 1374) from tobacco, has the composition of malonic acid, and is probably identical therewith. It crystallises in small scales, forms insoluble lead- and silver-salts, and is resolved by heat into carbonic anhydride and acetic acid.

MALT. Grain, chiefly barley, which has become sweet from the conversion of its starch into sugar, by an incipient growth or germination artificially induced, called malting. (See Beer, i. 527; also *Ure's Dict. of Arts*, &c. iii. 18)

MALTHA. The mineral tallow of Kirwan, said to have been found on the coast of Finland. It resembles wax. Its specific gravity is 0·77. It is white, brittle, stains paper like oil, melts with a moderate heat, and burns with a blue flame and much smoke. It dissolves readily in oil, and imperfectly in hot alcohol.

MALTHACITE. See Montmorillonite.

MALTOSE. This name is given by Dubrunfaut (Ann. Ch. Phys. [3] xxi. 178), to the sugar produced from starch-paste by the action of malt or diastase. It resembles dextro-glucose in crystalline form and most other respects, but its dextrorotatory power is, according to Dubrunfaut, three times as great as that of dextro-glucose, and not stronger in a recently prepared solution than after the lapse of several hours (ii. 858). It appears also to be less easily altered by alkalis. It is converted into dextro-glucose by boiling with dilute sulphuric acid.

MANCINITE. A brown mineral from Mancino, near Leghorn, consisting, according to Jacquot (Ann. Min. [3] xix. 703), of sesquisilicate of zinc, $2Zn^2O.3SiO^2$. It is plumose and shining, with two unequal cleavages inclined to one another at 92°.

MANDELIC ACID. *Formo-benzoilic acid*, $C^{16}H^{16}O^6$.—This acid, which contains the elements of bitter almond oil and formic acid, $C^{16}H^{16}O^6 = 2C^7H^6O + 2CH^2O^2$, and is related to benzoic acid (so far at least as composition is concerned) in the same manner as lactic to acetic acid, was discovered by Winckler (Ann. Ch. Pharm. xviii. 310), who obtained it by heating bitter almond water with hydrochloric acid, the hydrocyanic acid contained in the liquid being then resolved into ammonia and formic acid, which, at the moment of its formation, unites with the bitter almond oil (Liebig, Ann. Ch. Pharm. xviii. 89). It is also produced by the action of fuming sulphuric acid on bitter almond oil (Laurent, Ann. Ch. Phys. [2], lxv. 202), and by heating amygdalin with fuming hydrochloric acid. (Wöhler, Ann. Ch. Pharm. lxvi. 238.)

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* The cyanacetic ether was obtained by the action of chloracetic ether on cyanide of potassium, or of iodacetic ether on cyanide of silver.

Preparation.—Bitter almond water—obtained by distilling 80 oz. of bitter almond paste with 90 lbs. of water till 160 oz. have passed over, then taking 80 oz. of this liquid, and shaking up the distillate with the bitter almond oil—is mixed with 4 oz. of hydrochloric acid of specific gravity 1·12, and evaporated to dryness over the water-bath, till all the hydrochloric acid is expelled. The yellowish crystalline residue, smelling slightly of bitter almonds, leaves pure sal-ammoniac when treated with cold ether; and the ethereal solution yields by spontaneous evaporation a slightly yellow crystalline mass, which, when treated with water, leaves a resinous flocculent body having the odour of bitter almonds. The aqueous solution is transparent and colourless, and contains pure mandelic acid, which crystallises on evaporation (Winckler). —2. When bitter almond oil is treated with one-third of its volume of fuming sulphuric acid, heat is evolved, the liquid becomes brown and thick, and solidifies in a compact mass on cooling. The mass, when treated with water, yields an upper semi-solid layer containing undecomposed bitter almond oil and stilbylous acid, and a lower layer containing mandelic acid and excess of sulphuric acid; the mandelic acid crystallises from the latter on cooling (Laurent).—3. A solution of amygdalin in hydrochloric acid is evaporated over the water-bath, and the syrupy mass treated with ether, which dissolves the mandelic acid. On evaporating the solution, the mandelic acid crystallises. (Wöhler, Liebig.)

Properties.—Mandelic acid forms a scaly crystalline mass (Winckler). It crystallises sometimes in rhombic needles, sometimes in rhomboïdal plates, frequently having their acute angles truncated (Laurent); in plates belonging to the rhombic system (J. Heusser, Pogg. Ann. xciv. 637). It has a very faint odour of sweet almonds, and a strong acid taste, with a somewhat styptic after-taste. It melts easily, with loss of water, into a yellow oil, which, on cooling, solidifies to a translucent gum (Winckler). When a solution of mandelic acid in strong hydrochloric acid is evaporated at a temperature above 100°, it becomes amorphous, and afterwards forms a solution with a small quantity of water, but is precipitated by a larger quantity in the form of a heavy yellowish oil (Wöhler). The acid is very soluble in *water*, *alcohol*, and *ether*.

Decompositions. The acid, *heated* above its melting point, diffuses an agreeable odour, recalling those of white-thorn blossoms, hyacinth, and gum benzoïn. Heated in a distillatory apparatus to a temperature short of carbonisation, it is converted into a dark brown, resinous, balsamic mass, which dissolves sparingly in water, but readily in alkalis and in alcohol. A large quantity of bitter almond oil passes over at the same time. The acid burns with a red, smoky flame, leaving a bulky, easily combustible charcoal (Winckler). When it is boiled with *nitric acid*, as long as nitrous fumes continue to escape, the formic acid is decomposed, and the bitter almond oil is converted into benzoic acid, which crystallises on addition of water (Liebig). When *chlorine gas* is passed through an aqueous solution of mandelic acid, an oil smelling like chloride of benzoyl separates at first; and if potash be then added, and the passage of the chlorine continued till this oil has completely disappeared, the solution, when subsequently treated with acid, gives off carbonic anhydride and deposits benzoic acid in the form of a crystalline magma (Liebig). The acid dissolves in *oil of vitriol*, and the solution, when gently heated, gives off carbonic oxide (Liebig). The aqueous solution, boiled with *peroxide of manganese*, yields carbonic anhydride and bitter almond oil. (Liebig.)

Mandelates.—The acid neutralises bases completely, and expels carbonic acid from its compounds. (Winckler.)

Mandelate of Ammonium.—This salt is obtained by slightly supersaturating the aqueous acid with ammonia, and leaving the solution to evaporate. It is very difficult to crystallise, and generally forms a yellowish-white mass. It has a very mild taste. When heated, it decomposes in the same manner as the free acid. It dissolves in the smallest quantity of water, and readily in alcohol. (Winckler.)

Mandelate of Barium, obtained by decomposing carbonate of barium with mandelic acid, crystallises readily in small, tolerably hard needles. It is much less soluble in water than the potassium-salt. (Winckler.)

Mandelate of Copper.—A solution of sulphate of copper, precipitated by mandelate of potassium, yields a fine light-blue powder, which, when heated, gives off a large quantity of bitter almond oil.

Mandelate of Lead is precipitated as a white, finely crystalline powder, on adding mandelate of potassium to neutral acetate of lead. When heated, it behaves like the copper-salt. It is scarcely soluble in water. (Winckler.)

Mandelate of Magnesium crystallises readily. (Winckler.)

Mercuric Mandelate is obtained by precipitating mercuric nitrate with mandelate of potassium. Its reactions closely resemble those of the copper-salt. (Winckler.)

Mandelate of Potassium.—Obtained by nearly neutralising carbonate of potassium with the aqueous acid, evaporating to dryness, exhausting the dry mass with alcohol, and leaving the alcoholic solution to evaporate. It is a white, soft, easily friable, soapy mass, having a very mild, scarcely saline taste, faintly resembling that of sweet almonds. It decomposes like the free acid when heated, takes fire easily and burns away completely, leaving pure carbonate of potassium. It dissolves very readily in water and alcohol. (Winckler.)

Mandelate of Silver, obtained by precipitating nitrate of silver with neutral mandelate of potassium, forms a white, heavy, crystalline powder, easy to wash. From its aqueous solution saturated at the boiling heat, it separates in rather hard crystals having a slight yellowish colour. It melts at a somewhat high temperature into a dark mass, and yields the same products of decomposition as the acid, leaving metallic silver. (Winckler.)

MANGAN-AMPHIBOLE. See Rhodonite.

MANGANESE. Synonymes. *Manganese, Mangan, Manganium.* Symbols and Atomic Weights, Mn = 27·5; Mmn or M̶n = *55.*

History.—Black oxide of manganese, a substance long used to decolorise glass, and called *magnesia nigra*, from its resemblance to the loadstone, was formerly included among the ores of iron. It was, however, proved by the researches of Pott in 1740, of Kaim and Winterl in 1770, and of Scheele and Bergmann in 1774, that the metal contained in this mineral is distinct from iron, and possesses characters peculiar to itself. The metal itself was first eliminated by Gahn. Chevillot and Edwards, in 1818, pointed out that *mineral chameleon*—a substance discovered some considerable time before—contained a peculiar acid of manganese. Forchhammer, in 1820, distinguished two acids of manganese; and Mitscherlich, in 1832, fully confirmed the distinction.

Manganese occurs chiefly in the form of peroxide, known as black oxide of manganese; also as manganic and manganoso-manganic oxide; as sulphide, carbonate, silicate, and titanate; in small quantities also, as colouring matter in many siliceous minerals and in very minute quantity in the ashes of plants and in the bones of animals.

Preparation of the metal.—1. Hydrogen and charcoal at a red heat reduce the superior oxides of manganese to protoxide, but do not eliminate the metal; but at a white heat charcoal deprives the metal of the whole of its oxygen. The following process, recommended by John (*Gehlen's Journal für Chemie und Physik*, iii. 452), is commonly used for the reduction of manganese. A finely-divided oxide of manganese, obtained by calcining the carbonate in a well-closed vessel, is mixed with oil and ignited in a covered crucible, so as to convert the oil into charcoal. After several repetitions of this treatment, the carbonaceous mass is reduced to powder, and made into a firm paste by kneading it with a little oil. Finally this paste is introduced into a crucible lined with charcoal (*creuset brasqué*, p. 388), the unoccupied portion of which is filled up with charcoal powder. The crucible is first heated merely to redness for half an hour, to dry the mass and decompose the oil, after which its cover is carefully luted down, and it is exposed for an hour and a half to the most violent heat of an air-furnace that the crucible itself can support without undergoing fusion. The metal is obtained in the form of a semi-globular mass or button in the lower part of the crucible, but not quite pure, as it contains traces of carbon and silicium derived from the ashes of the charcoal. By igniting the metal a second time in a charcoal crucible, with a portion of borax, John obtained it more fusible and brilliant, and so free from carbon that it left no black powder when dissolved in an acid.

2. C. Brunner (Ann. Ch. Pharm. cii. 330; Jahresb. 1857, p. 201) obtains manganese by reducing the chloride or fluoride with sodium, in a manner similar to Deville's process for the reduction of aluminium: *a.* 2 pts. fluoride of manganese, and 1 pt. sodium are arranged in alternate thin layers in a hessian crucible; the mixture is well pressed, and covered with chloride of sodium; and over the whole is placed a layer of fluor-spar in small pieces (to prevent spirting). The crucible, with the cover on, is then heated in a blast furnace, first gently, then, when the commencement of the action is indicated by a hissing noise, to bright redness for a quarter of an hour, after which, all the apertures of the furnace are closed, and the whole is left to cool. If the heat

has been strong enough, the manganese is found in a fused mass at the bottom of the crucible; if not, it must be heated again under a layer of chloride of sodium or potassium, mixed with $\frac{1}{10}$ of nitre (borax attacks it too strongly).

β. Instead of fluoride of manganese, a mixture of equal parts of chloride of manganese and finely-pulverised fluor-spar may be used, and reduced with sodium in the manner above described.

Manganese may be obtained in the pulverulent state by heating its amalgam (p. 802) in a tube filled with vapour of rock-oil. (Giles.)

Properties.—Manganese, obtained by reduction of either of its oxides with charcoal, is a greyish-white metal having the aspect of cast iron, very soft and brittle, with a fine-grained structure, and is easily split. Specific gravity 8·013 (John). Feebly magnetic. Melts only at the strongest heat of a blast furnace. It oxidises quickly when exposed to the air, and must, therefore, be kept under rock-oil, or in sealed tubes. It decomposes water slowly at ordinary temperatures, and dissolves easily, with evolution of hydrogen, in hydrochloric or dilute sulphuric acid. It does not reduce any simple metallic salts, except the salts of silver and gold, and even then the reduction is very slight.

The metal obtained from the chloride or fluoride by Brunner's process, has also the aspect of cast iron, and is very brittle, but it is not magnetic [? what power was used in testing it]; has a specific gravity of only 7·138 to 7·206; is hard enough to scratch and cut glass like a diamond; may be polished; and does not tarnish, even in moist air, at ordinary temperatures; when heated on platinum-foil, it becomes coloured like steel, and covered with a brown film of oxide. Under water, it oxidises slowly at ordinary temperatures, more quickly at the boiling heat, with scarcely perceptible evolution of hydrogen. When immersed in strong sulphuric acid, it eliminates but a small quantity of hydrogen at ordinary temperatures, but dissolves when heated, with evolution of sulphurous anhydride. In dilute sulphuric acid it dissolves readily, even at ordinary temperatures; also in nitric acid, in very dilute hydrochloric acid, and in acetic acid.

H. Deville (Compt. rend. xliv. 673) attributes the differences between the manganese prepared by Brunner's method, and that obtained by reducing either of the oxides with charcoal, to the presence, in the former, of impurities derived from the rock-oil adhering to the sodium, and to silicium from the fluor-spar. Wöhler found, indeed, that Brunner's manganese, when dissolved in hydrochloric acid, left a not inconsiderable residue of hydrated oxide of silicium; and Brunner himself afterwards found that this residue, from 12 samples obtained in different preparations, varied from 1·6 to 6·8 per cent. By fusing the coarsely-pulverised metal with twice its weight of chloride of sodium containing 1 per cent. of chlorate of potassium, the quantity of silicium could be reduced to 0·1 per cent.; but Brunner did not find that this reduction in the proportion of the silicium made any difference in the colour, fusibility, hardness, or lustre of the metal. (See MANGANESE, SILICIDE OF.)

Manganese enters as a base into two classes of compounds, namely, the manganous compounds, in which it is mono- or di-atomic, according to the atomic weight adopted; and the manganic compounds, in which it is sesqui- or tri-atomic. It likewise enters as an acid-radicle into two classes of salts, the manganates and permanganates. Examples of these compounds are given in the following table:—

Manganous chloride . .	$MnCl$	$= 27·5 + 35·5$	$= 63$
or	$MmnCl^2$	$= 55 + 2 . 35·5$	$= 126$
Manganous oxide . .	Mn^2O	$= 2 . 27·5 + 16$	$= 71$
or	$MmnO$	$= 55 + 16$	$= 71$
Manganic chloride . .	Mn^2Cl^3	$= 2 . 27·5 + 3 . 35·5$	$= 161·5$
or	$MmnCl^3$	$= 55 + 3 . 35·5$	$= 161·5$
Manganic oxide . . .	Mn^4O^3	$= 4 . 27·5 + 3 . 16$	$= 158$
or	Mmn^2O^3	$= 2 . 55 + 3 . 16$	$= 158$
Manganate of potassium .	$MnKO^2$	$= 27·5 + 39·2 + 2 . 16$	$= 98·7$
or	$MmnK^2O^4$	$= 55 + 2 . 39·2 + 4 . 16$	$= 197·4$
Permanganate of potassium	Mn^2KO^4	$= 2 . 27·5 + 39·2 + 4 . 16$	$= 158·2$
or	$MmnKO^4$	$= 55 + 39·2 + 4 . 16$	$= 158·2$

Manganese also combines with chlorous elements in other proportions, *e.g.* the peroxide = $MmnO^2$.

MANGANESE, ALLOYS OF. The compounds of manganese with other metals are not of much importance. It unites with cobalt, nickel, copper (ii. 43), iron (iii. 368), and gold, forming white, brittle, and very refractory alloys.

An alloy of manganese and aluminium, $MnAl^3$, is obtained by melting together 10 pts. anhydrous chloride of manganese, 30 pts. of a mixture of the chlorides of potassium and sodium in atomic proportions, and 15 pts. aluminium, and treating the resulting regulus with dilute hydrochloric acid. It forms a dark grey crystalline powder, of specific gravity 3·402, insoluble in cold, but easily soluble in hot concentrated nitric acid; also, in concentrated hydrochloric acid; it is decomposed by caustic soda-ley, even when dilute, the aluminium dissolving out. (Wöhler, Ann. Ch. Pharm. cxv. 102.)

An amalgam of manganese is obtained by reducing a solution of the chloride with sodium-amalgam. (Giles, Phil. Mag. [4] xxiv. 328.)

MANGANESE, ARSENIDE OF. Mn^2As or MmnAs.—This compound occurs as a natural mineral, *Arsenical manganese* or *Kaneite*, in botryoïdal masses, or amorphous with foliated or granular structure. Specific gravity 5·55. Hard. Greyish-white. Becomes covered with a blackish-grey powder when exposed to the air. Melts on platinum-foil, and combines with the platinum. Before the blowpipe, it burns with a blue flame, garlic odour, and emission of white fumes of arsenious anhydride. It dissolves completely in nitromuriatic acid, and in a large quantity of nitric acid. Contains, according to Kane's analysis (Pogg. Ann. xix. 145), 45·5 per cent. manganese, 51·8 arsenic, and a trace of manganese (= 97·3), the formula requiring 42·75 Mn and 57·25 As. The specimen examined was supposed to be from Saxony.

MANGANESE, BROMIDE OF. MnBr or $MmnBr^2$.—The anhydrous bromide is obtained as a pale red fused mass, by heating the pulverised metal in bromine-vapour. By dissolving the carbonate in hydrobromic acid and evaporating, the hydrated bromide, $MnBr.2H^2O$, is obtained in small, red, deliquescent needles, isomorphous with the ordinary form of hydrated manganous chloride (Marignac, see p. 804). The crystals, when carefully heated in a close vessel, give off their water of crystallisation, and leave the anhydrous bromide; and this, when ignited in contact with the air, gives off bromine-vapour, and leaves manganoso-manganic oxide. It is decomposed by sulphuric acid, the bromine going off partly in the free state, partly as hydrobromic acid. (Löwig.)

MANGANESE, CHLORIDES OF.—*a. Manganous Chloride*, MnCl or $MmnCl^2$. This compound is formed by direct combination, the finely-divided metal taking fire when thrown into chlorine gas. It is also produced by passing dry hydrochloric acid gas over manganous carbonate or the red oxide, heated first gently, afterwards to low redness, the process being continued till the gas is no longer absorbed, and the product forms a clear, colourless liquid. The air must be carefully excluded during the whole of the reaction; the mass must be left to cool in the current of hydrochloric acid; and the excess of the latter finally expelled by a stream of dry air.

Manganous chloride obtained by this process, or by heating the hydrated chloride, is a pale rose-coloured mass, having a lamino-crystalline structure. According to H. Rose, it may be obtained in yellow crystals, by passing chlorine gas over a strongly ignited mixture of manganous oxide and charcoal; also, by exposing a mixture of the peroxide with sal-ammoniac to a gradually increasing heat. Manganous chloride melts to an oily liquid at a dull red heat, but does not volatilise at a temperature above the melting point of glass. It is not decomposed by heat alone, if air be excluded, but when ignited in moist air, it gives off hydrochloric acid, and leaves manganoso-manganic oxide. *Hydrogen gas* does not act upon it at a red heat, but *phosphoretted hydrogen* decomposes it, forming phosphide of manganese and hydrochloric acid. When heated with *sulphur*, it is partly converted into sulphide of manganese. When *water* is poured upon the anhydrous chloride, it becomes hot, and dissolves very easily. It is very deliquescent.

Hydrated Chloride, $MnCl.2H^2O$ or $MmnCl^2.4H^2O$.—The protoxide and carbonate of manganese dissolve readily in cold hydrochloric acid; and the higher oxides, with evolution of chlorine, when heated therewith, the product being in all cases manganous chloride. It is contained, together with ferric chloride and other substances, in the waste-liquor of the preparation of chlorine by heating the common black oxide of manganese with hydrochloric acid; and as this liquid accumulates very quickly in chemical laboratories, it may, after proper purification, be advantageously used as a source of the pure chloride, and thence of the other preparations of manganese. The iron, which is the chief impurity, may be removed by boiling down considerably, to expel the excess of acid, afterwards diluting with water, and boiling again with carbonate of manganese, which salt precipitates the whole of the sesquioxide of iron, forming chloride of manganese with its acid. If about one-fourth of the impure solution of chloride of manganese be reserved, and precipitated by carbonate of sodium, a quantity of carbonate of manganese will be obtained, which is sufficient to precipitate the iron from the other three-fourths of the liquid, and may be used for that purpose after it has been washed. The iron may likewise be separated by evaporating the solution of the impure chloride to dryness, heating the residue to low redness in a crucible, as long as hydrochloric acid continues to escape; then leaving it to cool, exhausting with boiling water, and filtering. The hydrated chloride of iron is resolved by the heat into hydrochloric acid and sesquioxide, while the chloride of manganese remains unaltered, and is easily dissolved out by water, all the iron remaining behind (**Everitt**, Phil. Mag. [3] vi. 493). Chloride of manganese, when free from iron, is precipitated white, without any shade of blue, by ferrocyanide of potassium, and of a pure flesh-red colour, by sulphide of ammonium: the latter test is the most delicate, the slightest trace of iron imparting a perceptible blackness to the precipitated sulphide. By precipitating the whole of the solution with sulphide of ammonium, the manganese may be freed from barium, calcium, and other impurities present. If copper is present, it must be removed by sulphydric acid, before precipitating with sulphide of ammonium.

The solution of chloride of manganese, obtained by either of these processes, yields by cooling, or by spontaneous evaporation, between 15° and 20°, crystals of the hydrated chloride having the composition above indicated. They are monoclinic, but the determinations of their form by different observes do not agree. According to **Schabus** (*Beschreibung der Krystallgestallen*, &c.), they exhibit the combination ∞P . [∞P∞] . [P∞]. Ratio of clinodiagonal, orthodiagonal, and principal axis = 0·4101 : 1 : 0·8331. Angle of inclined axes = 54° 50′; ∞P : ∞P in the clinodiagonal principal section = 142° 56′; [P∞] : [P∞] = 111° 20′. But, according to **Rammelsberg** (*Krystallographische Chemie*, p. 45), and **Marignac** (*Recherches sur les formes crystallins de quelques composés chemiques*, Genève, 1855; Compt. rend. xlii. 288), the clinod., orthod., and principal axis, are to one another as 1·1525 : 1 : 0·6445, and the angle of the inclined axes is 80° 35′. Angle ∞P : ∞P in the clinodiagonal principal section = 82° 40′; [P∞] : [P∞] = 115° 5′; ∞P∞ : [P∞] = 97° 15′.—**Marignac** has since found (Compt. rend. xlv. 650), that crystals of the same composition, but of different form, isomorphous with those of hydrated ferrous chloride, $FeCl.2H^2O$, are sometimes obtained when a solution of manganous chloride, supersaturated by evaporation at a high temperature, is left to stand for some time at a temperature between 0 and + 6° in a vessel covered with bibulous paper. These crystals are also monoclinic, but the angle of their inclined axes is 69° 14′. They exhibit the combination 0P . +P . −P . [½P∞]. Angle +P : +P in the clinodiagonal principal section = 86° 0′; −P : −P in the same = 105° 36′; +P : −P in the principal orthodiagonal section = 103° 59′ : oP : +P = 103° 30′; oP : −P = 126° 30′; oP : [½P∞] = 142° 30′. Hydrated manganous chloride is therefore dimorphous. It must be observed, however, that the crystals last described are of rare occurrence, the solution, even when evaporated under the peculiar circumstances just mentioned, generally yielding the ordinary crystals previously described according to the determinations of Marignac and Rammelsberg. As the crystals measured by Schabus are decidedly different from both, it is probable that he examined a different hydrate.

The crystals ($MmnCl^2.4H^2O$) placed over oil of vitriol, either in vacuo or in a receiver containing air, lose 2 at. water at ordinary temperatures (**Graham**). At 25 they become white and opaque (**John**); between 25° and 37° they give off hygroscopic water with decrepitation, and become hard; at 37·5° they become tough; at 50° semi-fluid; and at 87·5 they form a mobile liquid, which boils at 106°. If the mass be kept for some time at a temperature near 100°, it gives off 28 per cent. (3 at.) of water, and leaves a white powder, which retains 1 at. water. (**Brandes.**)

Both the anhydrous and the hydrated chloride deliquesce rapidly in the air, one part of the crystals absorbing 1·2 parts of water. One part of the crystallised salt dissolves at 10° in 0·66 parts; at 31·25° in 0·37; and at 62·5, 87·5° and 106°, equally, in 0·16 parts of water (**Brandes**). The solution has a light rose colour, and thin, syrupy consistence.

The salt dissolves readily in alcohol, but is insoluble in ether and oil of turpentine. The alcoholic solution of the hydrated salt is green, and yields on cooling colourless crystals, still containing 4 at. water. The anhydrous chloride, dissolved to saturation in boiling absolute alcohol, crystallises out on cooling, and the remaining solution evaporated in vacuo yields an additional quantity of crystals, containing 0·4 of their weight of alcohol.

A solution of manganous chloride is not altered by passing chlorine through it; but if chloride of potassium, chloride of barium, &c., be added at the same time, a precipitate of hydrated peroxide of manganese is formed (**Sobrero** and **Selmi**, Ann. Ch. Phys. [3] xxxix. 161). According to **Millon** (Jahresb. 1849, p. 254), the same oxidation is produced by chlorine water which has been exposed to sun-light, and therefore contains hydrochloric and hypochlorous acids.

Manganous chloride forms two crystalline double salts with *chloride of ammonium*. One of these, $MmnCl^2.2NH^4Cl$, forms cubical crystals containing 1 at. water according to Rammelsberg, and 2 at. according to v. Hauer. The crystals when ignited leave manganoso-manganic oxide in microsopic pyramids resembling hausmannite. The other double salt, $MmnCl^2.NH^4Cl.2H^2O$, forms monoclinic crystals (Hautz). Solution of manganous chloride containing chloride of ammonium yields, on addition of ammonia and exposure to the air, a precipitate of hydrated manganoso-manganic oxide. (Otto.)

A compound of *manganous chloride and mercuric cyanide*, $MmnCl^2.HhgCy$, is obtained, by spontaneous evaporation of a solution containing the two salts in atomic proportion, in colourless four-sided tablets, which effloresce quickly in the air, and are very soluble in water. (Poggiale.)

β. *Manganic Chloride*, Mn^2Cl^3 or $MmnCl^3$ is not known in the solid state, but when finely divided manganoso-manganic or manganic oxide is added by small portions at a time, in order to avoid rise of temperature, to cold concentrated aqueous hydrochloric acid, a brown solution is formed, which slowly becomes colourless at ordinary temperatures, and more rapidly when heated or exposed to sunshine—chlorine being evolved and manganous chloride produced: hence the solution dissolves metals as readily as chlorine-water. It likewise converts sulphurous and sulphydric acids into sulphuric, and tartaric into carbonic acid. The addition of water in large quantities precipitates manganic oxide, and gives rise to the formation of manganous chloride. (Forchhammer.)

When chlorine is passed into a solution of 1 pt. manganous chloride in 19 pts. water cooled to + 5°, the liquid gradually solidifies to a yellow crystalline mass which, however, melts for the most part, on slight rise of temperature (John). The crystals thus obtained deliquesce very readily in the air, and are decomposed by gentle heating, just like the solution of manganous oxide in hydrochloric acid.

γ. *Perchloride of Manganese*, Mn^2Cl^7? When sulphuric acid is added to a green solution of potassic manganate till the liquid turns red; the solution then evaporated to dryness; the residue, consisting of sulphate and permanganate of potassium, dissolved in strong sulphuric acid; the solution introduced into a tubulated retort; and fragments of fused chloride of sodium added as long as coloured vapours are evolved,—the copper-coloured or green vapours which distil over, condense entirely in a tube attached to the retort and cooled down to − 15° or − 20°, forming a greenish-brown liquid. The vapours, when brought in contact with moist air in a wide tube, produce a dense rose-coloured cloud, and form on the sides of the tube, with evolution of hydrochloric acid, a deposit of purple-red permanganic acid (Dumas, Ann. Ch. Phys. [2] xxxvi. 81). H. Rose regards this compound as probably analogous to the chromate of trichloride of chromium.

MANGANESE, CYANIDES OF. See CYANIDES (ii. 253).

MANGANESE, DETECTION AND ESTIMATION OF.—1. *Reactions in the Dry Way*. All compounds of manganese, heated with borax or phosphorus-salt in the outer blow-pipe flame, form an amethyst-coloured bead containing manganoso-manganic oxide, which becomes colourless in the inner flame by reduction of that compound to manganous oxide. This reaction, when not disguised by the presence of other metals forming coloured beads, is extremely delicate, and serves to distinguish manganese from all other metals. Another reaction, equally characteristic, even more delicate, and not likely to be interfered with by the presence of other metals, is obtained by heating the substance under examination with two or three times its weight of carbonate of sodium and a little nitre, on platinum-foil in the outer blow-pipe flame. The smallest trace of manganese will then be indicated by the formation of green manganate of sodium. The best way of applying the heat is to direct the hottest part of the flame on the under side of the platinum-foil immediately beneath the mixture. In testing for traces of manganese in ores which are rich in iron, it is best to treat them with nitric acid, which dissolves the iron as ferric-salt; nearly saturate the solution with carbonate of sodium, and precipitate the iron with acetate of sodium; then saturate the filtrate with ammonia, add one drop of sulphide of ammonium, and test the precipitated sulphide by fusion with nitre and carbonate of sodium, as above.

2. *Reactions in Solution*.—*a. Of Manganous Salts*.—These salts have a pale rose tint, which is not destroyed by sulphurous or hydrochloric acid, and must therefore be considered as characteristic. When the solution is colourless, as is sometimes the case, the fact is explained, according to Görgeu, by the presence of a salt of iron, nickel, or copper, the green or blue tint of the latter metals producing a white or scarcely perceptible violet tint, when combined with the rose colour of a manganous salt.

Sulphydric acid forms no precipitate in neutral solutions of manganous salts containing any of the stronger acids. In a neutral solution of the acetate, a flesh-coloured precipitate is formed after some time; but not if the solution contains free acetic acid. *Sulphide of ammonium* forms, in neutral solutions of manganous salts, a flesh-coloured precipitate of hydrated sulphide of manganese, insoluble in excess of sulphide of ammonium, but readily soluble in acids. When exposed to the air, it turns brown on the surface, from oxidation. This reaction is quite characteristic, no other metal giving anything like it; a very small trace of iron or cobalt, however, colours the precipitate black.

Caustic alkalis, added to solutions of manganous salts, throw down the protoxide of manganese in the form of a white hydrate, which soon absorbs oxygen from the air, and becomes brown; when collected on a filter and washed, it ultimately changes into a blackish-brown powder, which is the hydrate of the sesquioxide. A similar change is instantaneously produced by the action of chlorine-water upon the white hydrate, or by the addition of chloride of lime to a salt of the protoxide of manganese; but then the hydrated peroxide is formed. *Ammonia* precipitates the white hydrate from neutral manganous solutions; in solutions containing free acid or ammoniacal salts, it gives no precipitate; but if sufficient ammonia is added, the solution, on exposure to the air, gradually deposits all the manganese as brown sesquihydrate. The *alkaline monocarbonates* precipitate white carbonate of manganese, which does not turn brown in the air, and dissolves sparingly in a cold solution of sal-ammoniac. *Acid carbonate of potassium* precipitates a strong solution immediately, and renders a dilute solution slightly turbid; but if the solution contains a free acid, so that an excess of carbonic acid is set free, no precipitate is formed. The *earthy carbonates* do not precipitate manganous salts. *Alkaline phosphates, arsenates*, and *oxalates* give white precipitates.

Ferrocyanide of potassium forms in neutral solutions of manganous salts, a white precipitate, having a tinge of red, and soluble in free acids. *Ferricyanide of potassium* forms a reddish precipitate, insoluble in acids.

The least trace of a manganous salt may be detected by heating the solution with a little *dioxide of lead* (or red lead), and *nitric acid*, when an intense purple-red colour is produced, owing to the formation of permanganic acid, or, according to H. Rose, of manganic oxide. The colour is readily perceptible when the excess of lead-oxide has subsided. This is the most delicate test for manganese in the wet way. (W. Crum.)

All compounds of manganese, after boiling with hydrochloric acid, exhibit the reactions of manganous salts.

β. *Of Manganic salts.*—Solutions of manganic salts are red, and yield with *potash* a black precipitate of manganic hydrate, unless chloride of ammonium is present, in which case no precipitate is formed. They are very unstable, being reduced to manganous salts merely by heating, also by *hydrochloric, sulphurous*, or *nitrous acid*, or any *organic compound*, the liquid then becoming colourless. Sulphide of ammonium reduces them to manganous salts, and then precipitates the flesh-coloured sulphide.

γ. *Of Manganates.*—The manganates of the alkali-metals are soluble in water, forming green solutions, which, however, are very unstable, quickly turning red on exposure to the air, from formation of permanganic acid, and depositing the brown hydrated peroxide; this change is retarded by the presence of excess of alkali. *Nitric, sulphuric*, or *hydrochloric* acid, effects the change at once; with hydrochloric acid, the red solution gradually becomes brown, and, when heated, colourless, owing to the formation of manganous chloride. The solution is also decolorised by *sulphurous* and *sulphydric acids*, and other reducing agents.

δ. *Of Permanganates.*—The alkaline permanganates form solutions of a deep purple-red colour. They are very easily reduced by *organic compounds*, and by all reducing agents (e. g. *hydrochloric, sulphurous, arsenious, nitrous*, and *sulphydric acids, ferrous salts, stannous salts*, &c.), the solution first becoming green and ultimately colourless.

3. *Quantitative Estimation and Separation.*—The usual method of precipitating manganese from the solution of a manganous salt, is to add carbonate of sodium at the boiling heat. The precipitated carbonate of manganese is then well washed with boiling water, and calcined at a strong red heat, whereby it is converted into manganoso-manganic oxide, Mn^3O^4, containing 72·11 per cent. of manganese. If the solution contains a considerable quantity of ammoniacal salts, it must be evaporated, after mixing it with excess of carbonate of sodium, and the soluble salts dissolved out of the residue by water.

From the metals of Group I. (i. 217), manganese is separated by the non-precipitation of its sulphide from an acid solution by sulphydric acid. Its separation from the metals of Group II., which, like manganese itself, are precipitated by sulphide of ammonium and not by sulphydric acid, is more difficult.

The methods of separating manganese from iron have been already given under IRON (p. 386). The best is to precipitate the iron (previously brought into the ferric state by succinate or benzoate of ammonium) from a solution carefully neutralised with ammonia.

From **cobalt, nickel,** and **zinc**, manganese may be separated by mixing the solution with *acetate of sodium*, and saturating with *sulphydric acid gas*, which throws down the other metals, leaving the manganese in solution. In the case of cobalt and nickel, the solution must not contain much free acid. The separation thus effected is not very complete at first, but it may be rendered almost absolute by repeating the process two or three times. Other methods of separating manganese from cobalt are given under COBALT (i. 1046). One of the best is that which consists in converting the two metals into chlorides, and igniting them in a stream of *hydrogen*, which reduces the cobalt, and leaves the chloride of manganese undecomposed. The same methods may be used for separating manganese from nickel.

From **uranium**, manganese is separated by precipitating that metal as uranic oxide by means of *carbonate of barium*, which leaves all the manganese in solution. For the separation from **chromium**, see i. 915.

From the metals which are precipitated by sulphide of ammonium from their neutral solutions as hydrates, viz. those of the **earths proper**, also **cerium, lanthanum,** and **didymium**, manganese may be separated by mixing the solution with a sufficient quantity of *tartaric acid* to prevent the precipitation of those metals by an alkali, then adding excess of *ammonia*, and precipitating the manganese by *sulphide of ammonium*.

From **yttrium, thorium, zirconium, cerium, lanthanum,** and **didymium** it may also be separated by precipitating those metals with *oxalate of ammonium*, after adding sal-ammoniac to retain the manganese in solution; from **cerium** and its allied metals, also by sulphate of *potassium* (i. 833).

For the methods of separation from **titanium, tantalum,** and **niobium**, see those metals.

From **aluminium** and **glucinum**, manganese, if in small or moderate quantity only, may be separated by boiling the solution with *potash* in an open vessel. The manganese is then precipitated in the form of sesquioxide, while the alumina and glucina are dissolved by the potash. If, however, the proportion of manganese be considerable, this method cannot be used, because the oxide of manganese carries down with it considerable quantities of alumina and glucina. In this case the liquid must be mixed with sal-ammoniac, and the alumina and glucina precipitated by *ammonia* The precipitate, however, always contains small quantities of manganese, which must be separated by subsequent treatment with potash.

From **barium** and **strontium** manganese is easily separated by means of *sulphate of sodium* which throws down the barium and strontium as sulphates; also by *sulphide of ammonium*. From **calcium** and **magnesium** it is separated by *oxalate of ammonium*, which, if the solution be sufficiently dilute, precipitates the manganese alone in the form of sulphide. The separation from calcium may also be effected by means of *oxalate of ammonium*, after the addition of chloride of ammonium to keep the manganese in solution.

Manganese is separated from the **alkali-metals** by means of *carbonate of sodium* or *sulphide of ammonium*, which latter precipitates it in the form of sulphide. The sulphide is washed with water containing a small quantity of sulphide of ammonium; then redissolved in acid; and the manganese precipitated from the solution by carbonate of sodium.

4. *Valuation of Ores of Manganese.*—As the commercial value of manganese ores depends, not on the quantity of metal, but on that of the available oxygen contained in them, the mode of assaying them does not properly come under the estimation of manganese, but will be best considered in connection with the oxides of manganese. (See p. 814.)

5. *Atomic Weight of Manganese.*—The earlier determinations of this number by **Berzelius, J. Davy,** and **Forchhammer**, were either too high or too low. **Arfvedson** in 1818 (Schw. J. xlii. 202), by precipitating the solution of manganous chloride with nitrate of silver, found the atomic weight of manganese to be 28, that is to say, the same as that of iron. **Turner**, in the same year (Phil. Mag. [2] iv. 22), by a similar method, obtained the number 27·49, and by determining the quantity of manganous sulphate produced by treating a known quantity of manganous oxide with sulphuric acid, he found $Mn = 27·96$. **Berzelius** in 1830 (Pogg. Ann. xiv. 211) also, by precipitating manganous chloride with nitrate of silver, found that 4·20775 $MnCl$ gave 9·575 $AgCl$; whence, if $Ag = 108$ and $Cl = 35·5$, calculation gives $Mn = 27·5$. **Dumas**, in 1859 (Ann. Ch. Pharm. cxiii.), found, as a mean of five similar experiments, $Mn = 27·48$.

v. **Hauer** (Chem. Centr. 1857, p. 88) determined the atomic weight of manganese by converting anhydrous manganous sulphate into the corresponding sulphide. The quantity of oxygen in the sulphate was thus found, as a mean of nine experiments, to be 42·390 per cent. (from 42·351 to 42·428); whence $Mn = 27·49$.

The most exact of the preceding experiments appear to show that the atomic weight of manganese is 27·5 or 55, according as it is regarded as mono- or diatomic.

R. Schneider (Pogg. Ann. (1859) cvii. 655) has, however, obtained a much lower result: 1. By determining the quantity of water produced in the reduction of manganoso-manganic to manganous oxide by reduction with hydrogen: 2. By determining the ratio between the carbon and manganese in manganous oxalate. The first method gave as a mean, Mn = 27·01; the second 27·02. Schneider therefore regards 27 as the true atomic weight of manganese.

MANGANESE, EARTHY. This term is applied to oxides of manganese occurring in amorphous, loosely coherent masses (see p. 813).

MANGANESE, FLUORIDES OF. *Manganous fluoride*, MnF or $MmnF^2$, is obtained by dissolving the carbonate in excess of hydrofluoric acid. On evaporating the excess of acid, the salt separates in small, indistinct, amethyst-coloured crystals, which are insoluble in pure water, but dissolve in water containing free hydrofluoric acid. The fluoride is not decomposed by heat alone, but when heated with sodium, it yields metallic manganese (p. 801).

Manganic fluoride, Mn^2F^3 or $MmnF^3$, is obtained by digesting the sesquioxide or peroxide with excess of hydrofluoric acid. The resulting dark brown solution yields, by spontaneous evaporation, crystals of manganic fluoride, which are ruby-coloured by transmitted light, and yield a rose-coloured powder. They dissolve without decomposition in a very small quantity of water; but the solution is decomposed by dilution into a soluble acid fluoride and an insoluble basic compound or oxyfluoride. Ammonia, added to the solution, throws down manganic hydrate.

Perfluoride of Manganese, Mn^2F^7 or $MmnF^7$?—When a fused mixture of peroxide of manganese, hydrate of potassium, and chlorate or permanganate of potassium is mixed with half its weight of fluor-spar, and drenched with strong sulphuric acid, a yellow vapour is formed, which is decomposed and acquires a purple colour by contact with moist air, and corrodes glass, forming fluoride of silicium and permanganic acid. With water, it is resolved into hydrofluoric and permanganic acids, forming a purple solution, which remains unchanged in stoppered bottles, but, when evaporated, evolves oxygen gas and hydrofluoric acid vapour, and leaves a brown shining residue, from which water dissolves manganous fluoride, leaving a black insoluble basic salt. The solution also dissolves copper, mercury, and silver (not gold or platinum), forming fluorides, and at the same time becoming perfectly colourless. (Wöhler, Pogg. Ann. ix. 619; see also Dumas, Ann. Ch. Phys. [2] xxxvi. 82.)

MANGANESE, GREY. A term sometimes applied to manganite and pyrolusite (pp. 810, 811).

MANGANESE, IODIDES OF. *a. Manganous Iodide*, MnI or $MmnI^2$.—A solution of manganous carbonate in aqueous hydriodic acid leaves a white crystalline mass, having a somewhat styptic taste. When kept from contact of air, it may be fused without decomposition; but on the admission of air, it is resolved into vapour of iodine and manganous oxide. It deliquesces in the air, and dissolves readily in water, forming a colourless solution, which, on evaporation, deposits white needles. The solution, when exposed to the air, is slightly decomposed, depositing brown flakes. Bromine and chlorine, as well as concentrated nitric or sulphuric acid, set the iodine free. (Lassaigne.)

β. Manganic Iodide.—Very finely-pounded peroxide of manganese, agitated with cold aqueous hydriodic acid, yields a dark yellowish-red solution, which, when heated, evolves iodine, and is rapidly converted into manganous iodide.

MANGANESE, OXIDES OF. Manganese forms four oxides of definite composition, viz.:—

Protoxide or Manganous oxide	Mn^2O or $MmnO$
Manganoso-manganic oxide	Mn^3O^2 or Mmn^3O^4
Sesquioxide or Manganic oxide	Mn^4O^3 or Mmn^2O^3
Dioxide or Peroxide	Mn^2O^2 or $MmnO^2$.

The protoxide is a strong base, forming with acids a class of very stable salts: the sesquioxide is a weak base. Manganoso-manganic acid also dissolves without decomposition in certain acids. The peroxide, treated with acids, is resolved into manganous or manganic oxide and free oxygen.

There are also two or three other native oxides, intermediate in composition between the sesqui- and di-oxides, viz. *Varvacite*, *Newkirkite*, &c., but they are not very definite, and are probably mere mixtures. Besides these it is usual to enumerate two higher oxides, Mn^2O^3 and Mn^4O^7, which are the anhydrides corresponding to manganic and permanganic acid respectively: but they have not yet been obtained, and must therefore at present be regarded as merely hypothetical. (See MANGANIC ACIDS.)

Protoxide, or **Manganous oxide,** Mn^2O, or MmnO.—This oxide may be prepared by igniting manganous hydrate, carbonate, or oxalate, at a moderate heat in a closed vessel, or better in a stream of hydrogen, and allowing the product to cool in that gas. The best mode of preparation is, however, that recommended by Liebig and Wöhler (Pogg. Ann. xxi. 584), which consists in mixing equal parts of fused manganous chloride and carbonate of sodium with a small quantity of sal-ammoniac, heating the mixture till it fuses, and exhausting the fused mass with water when cold.

Manganous oxide is a greyish-green powder, which, according to Despretz, melts at the heat of a forge-fire to a fine green-coloured mass. By heating it to a cherry-red heat in hydrogen, mixed with a very small quantity of hydrochloric acid gas, Deville (Compt. rend. lii. 1264) obtained it crystallised in transparent regular octahedrons of an emerald-green colour, and adamantine lustre. It is not deoxidised by any heat, however great. Heated in sulphydric acid gas, it yields water and manganous sulphide. When it is fused with sulphur, sulphurous anhydride is evolved, and manganous oxysulphide remains behind.

Hydrated Manganous oxide, or *Manganous hydrate*, is obtained by precipitating a manganous salt with caustic potash, as a white, milky, flocculent precipitate, which, on exposure to the air, turns brown by oxidation, and is ultimately converted into manganic hydrate. The same change is produced immediately by chlorine-water, or the solution of a hypochlorite. If it be washed in an apparatus from which the air is excluded as completely as possible, then dried in a stream of hydrogen, and heated in that gas just sufficiently to drive off the water, the remaining protoxide is sometimes pyrophoric, and when a red-hot coal is laid upon it, it glows from the point of contact throughout its whole mass, and is converted into manganic oxide. According to H. Davy, the hydrate contains 24 per cent. water.

Both the oxide and hydrate dissolve readily in nitric, sulphuric, and hydrochloric acid, forming solutions of manganous salts.

Sesquioxide, or **Manganic oxide,** Mn^4O^3, or Mmn^2O^3.—This oxide occurs native, as *Braunite*, in obtuse quadratic pyramids, in which the principal is to the secondary axes as 0·985 : 1. Angle of the terminal edges = 109° 53′; of the lateral edges = 180° 39′. Cleavage perfect, parallel to P, none parallel to oP. It occurs also massive. Hardness = 6—6·5. Specific gravity = 4·75—4·818. Lustre submetallic. Streak and colour dark brownish-black. Fracture uneven. Brittle. Infusible before the blowpipe. It occurs in veins traversing porphyry at Oehrenstock near Ilmenau; at Eglersberg in Thuringia; also near Ihlefeld in the Hartz; at St. Marcel in Piedmont; in the isle of Elba; at Vizianagram in India; and in the state of Vermont (U. S.).

Analyses of Braunite.

Locality .	*Eglersberg.*	*Tellemark.*	*Elba.*	*St. Marcel.*
Analyst .	Turner.	Tonsager.	Becht.	Damour.
Sesquioxide of manganese . .	96·71	95·83	91·42	96·62
Sesquioxide of iron	. .	1·74	4·75	1·45
Baryta	2·26	. .	1·03	
Lime	. .	. .	. .	1·22
Water	0·95	2·19	2·08	
	99·92	99·76	99·28	99·64

The same oxide is obtained as a black powder by heating manganous nitrate, peroxide of manganese, or manganic hydrate to low redness, the hydrate perhaps yielding the most definite product. If the heat is too strong, the residue consists of manganoso-manganic oxide.

According to R. Schneider (Pogg. Ann. cvii. 605) all the lower oxides of manganese are converted into sesquioxide by strong ignition in oxygen gas.

From the experiments of Dittmar (Chem. Soc. J. xvii. 294) it appears that the composition of the product obtained by heating an oxide of manganese depends upon the tension of the oxygen in the surrounding atmosphere as well as on the temperature. By heating peroxide of manganese to bright redness in pure oxygen of various tensions, also in various mixtures of oxygen and nitrogen, and in pure nitrogen, it was found that when the tension of the oxygen was between 0 and 0·21 atmosphere, manganoso-manganic oxide was formed; but when the oxygen-tension was between 0·26 and 1 atmosphere, the sesquioxide was obtained. The exact limit of tension which determines the stability of one or the other oxide appears to vary with the temperature.

Manganic oxide when strongly ignited in a close vessel, or in the air, gives off oxygen, and leaves manganoso-manganic oxide. By boiling with nitric acid, or with dilute sulphuric acid, it is resolved into protoxide, which dissolves, and peroxide, which remains undissolved. Hot strong sulphuric acid reduces it to manganous oxide, and dissolves it, with evolution of oxygen gas. Hot hydrochloric acid dissolves it, with evolution of chlorine.

Hydrated Manganic oxide, or *Manganic Hydrate*, $Mn^4O^3.H^2O$, or $\left.\begin{matrix}Mmn'''\\H\end{matrix}\right\}O^2$. — This compound is found native, as *Manganite* or *Grey Manganese ore*, in veins traversing porphyry, at Ihlefeld, in the Hartz; at Ilmenau and Oehrenstock in Thuringia; in Aberdeenshire; at Undenaes in Sweden; and at Christiansand in Norway. It forms trimetric crystals, usually exhibiting the face ∞P with $\infty\breve{P}\frac{3}{2}$ and other vertical prisms, together with oP and $\breve{P}\infty$, or a pyramid $\breve{P}3$, &c. Ratio of axes, $a : b : c = 0{\cdot}8440 : 1 : 0{\cdot}5444$; $\infty P : \infty P = 80° 20'$; $\infty\breve{P}\frac{3}{2} : \infty\breve{P}\frac{3}{2} = 103° 23'$; $\breve{P}\infty : \breve{P}\infty = 65° 41'$. Also twins with plane of combination $\breve{P}\infty$. Cleavage very perfect, parallel to $\infty\breve{P}\infty$. The crystals are longitudinally striated and often grouped. The mineral also occurs columnar and granular. Hardness = 4. Specific gravity = 4·2—4·4. Lustre submetallic. Colour dark steel-grey to iron-black. Streak reddish-brown, sometimes nearly black. Opaque; minute splinters sometimes brown by transmitted light. Fracture uneven. Fusible before the blowpipe.

Analyses of Manganite.

	West Gothland.	*Ihlefeld.*		Calculated.
	Arfvedson.	Gmelin.	Turner.	$Mn^4O^3.H^2O$.
Manganese . . .	89·92	62·86	62·68	62·50
Oxygen . . .		27·64	27·22	27·27
Water	10·08	9·50	10·10	10·23
	100·00	100·00	100·00	100·00

Manganic hydrate is prepared artificially by exposing moist manganous hydrate to the air, or by passing chlorine, not to saturation, into water in which manganous carbonate is suspended, decanting the liquid, and digesting the brown residue still containing manganous carbonate, in cold very dilute nitric or acetic acid to remove the manganous oxide; when prepared by this latter process however, it is often mixed with hydrated peroxide.

Manganous hydrate artificially prepared is a light powder having a dark brown colour and capable of soiling very strongly. It gives off its water at a temperature above 100°. By boiling with moderately concentrated nitric acid, it is resolved into protoxide, which dissolves, and a residue of hydrated peroxide. (Berthier.)

Manganic oxide dissolves without decomposition in cold hydrochloric acid, forming manganic chloride. Strong sulphuric acid combines with it at temperatures a little above 100°, but does not form a solution. Dilute sulphuric acid does not dissolve it, unless manganous oxide is present, even in very small quantity, in which case a violet solution is formed. (Carius.)

A manganic sulphate may be prepared by mixing finely divided peroxide of manganese with monohydrated sulphuric acid to the consistence of a pulp, and gradually heating the mixture to 135°. It may be heated to 160° without decomposition, but is decomposed at higher temperatures into oxygen and manganous sulphate. It is also quickly reduced by organic substances, and decomposed by water, with separation of manganous hydrate (Carius, Ann. Ch. Pharm. xcviii. 53). But the most stable of the simple manganic salts is the phosphate, which dissolves in water without decomposition.

Generally speaking, however, manganic oxide does not form stable salts with acids, unless another base or protoxide is present: with sulphuric acid, for example it forms several double salts having the constitution of alums; thus there is a manganico-potassic sulphate found native on the shores of the Great Salt Lake (see SULPHATES).

Manganoso-manganic oxide, or **Red oxide of Manganese.** Mn^3O^2 or $Mmn^3O^4 = MmnO.Mmn^2O^3$.—This oxide occurs native, as *Hausmannite*, and together with other manganese ores, with porphyry, near Ilmenau in Thuringia and near Ihlefeld in the Hartz. The crystals are acute quadratic pyramids, in which the principal is to the secondary axes as 1·175 : 1. Angle P : P in the terminal edges = 105° 25'; in the lateral edges = 117° 54'. Cleavage basal, nearly perfect. It also forms twin-crystals, the face of combination being parallel to $P\infty$, the same kind of combination sometimes occurring between four individuals. Also granular, sometimes strongly coherent. Hardness = 5 to 5·5. Specific gravity = 4·722. Lustre submetallic. Colour brownish-black. Streak chestnut-brown. Opaque. Fracture uneven. Infusible before the blowpipe.

Analyses of Hausmannite.

	Ihlefeld. Turner.	*Ilmenau.* Rammelsberg.
Red oxide of manganese	98·902	99·44
Oxygen	0·215	0·05
Baryta	0·111	0·15
Silica.	0·337	
Water	0·435	
	100 00	99·64

This oxide is the most easily obtained by artificial means of all the oxides of manganese, being always produced when manganous oxide, nitrate, or carbonate, is strongly ignited in contact with the air, or when either of the higher oxides is subjected to very strong ignition. Metallic manganese, exposed to moist air at ordinary temperatures, evolves hydrogen gas of a peculiar odour, and is converted into a reddish-brown powder, which is a mixture of manganese containing charcoal and silicium, with manganoso-manganic oxide, since it dissolves in hydrochloric acid, with evolution of hydrogen gas, and forms a brown solution, which, when heated, becomes colourless and gives off chlorine. The oxidation takes place more rapidly, in proportion as the manganese is more free from charcoal, and the air is warmer and contains more moisture. If the metal is heated in the air, the conversion into manganoso-manganic oxide takes place more rapidly, but without incandescence; in oxygen gas, the finely-divided metal becomes ignited. The red oxide is also produced, with evolution of hydrogen, by heating the protoxide in a stream of aqueous vapour. It is a reddish-brown or cinnamon-coloured powder, which turns black when heated, but recovers its original colour on cooling. When heated to whiteness with charcoal, it is reduced to metallic manganese. By boiling with dilute sulphuric or with nitric acid, it is resolved, like the sesquioxide, into protoxide and peroxide; hot strong sulphuric acid dissolves it as manganous sulphate, with liberation of oxygen; hot hydrochloric acid, with liberation of chlorine. It dissolves without decomposition in a hot, very strong solution of phosphoric acid, and in cold concentrated sulphuric, hydrochloric, oxalic, or tartaric acid, but only in small quantity, and without neutralising the acid. The solutions, treated with caustic potash, yield a brown precipitate, perhaps consisting of manganoso-manganic hydrate. Heat, and the addition of water, or of deoxidising agents, converts these salts (the phosphate excepted) into salts of manganous oxide, with a large excess of acid.

Dioxide or Peroxide. Mn^2O^3 or $MmnO^2$.—This oxide occurs in nature as *Pyrolusite* or *Polyanite*, in trimetric crystals exhibiting the combination $\infty\breve{P}\infty \,.\, \infty P \,.\, \infty\bar{P}\infty \,.\, oP \,.\, \frac{1}{2}\breve{P}\infty$. Ratio of axes $a : b : c = 0·776 : 1 : 1·066$. Angle $\infty P : \infty P = 93° 40'$. Also columnar, often divergent; also granular, massive, and frequently in reniform coats; often soils. Hardness = 2 to 2·5. Specific gravity = 4·819 (Turner); 4·97 when pure. Lustre metallic. Colour iron-black, dark steel-grey, sometimes bluish. Streak black. Opaque. Rather brittle. Infusible alone before the blowpipe; gives off oxygen on charcoal. It is a valuable ore of manganese, and is extensively worked at Eglersberg, Ilmenau, and other places in Thuringia; also at Vorderehrensdorf near Mährisch-Trübau in Moravia, which place affords annually many tons of the ore. It also occurs in Devonshire, and with psilomelane in many parts of the United States.

Analyses of Pyrolusite.

Locality .	*Devonshire.*	*Eglersburg.*	*Ihlefeld.*	*Ilmenau.*	*Undenaes.*	*Tarn.*	*Krettnich.*	Calculated. Mn^2O^2.
Analyst .	Turner.			Schefler.	Arfvedson.	Dufresnoy.	Riegel.	
Red oxide of manganese	85·62	84·05	85·62	87·0	83·56	72·5	86·00	87·74
Oxygen . . .	11·60	11·78	11·60	11 6	14·58	9·8	11·45	12·26
Sesquioxide of iron .	. .	. .	. .	1·3	. .	4·2	0·40	
Alumina . . .	. .	. .	. .	0·3				
Baryta . . .	0·67	0·53	0·66	1·2				
Lime	. .	. .	. .	0·3	. .	. .	trace	
Silica	0·55	0·51	0·55	0·8	. .	1·4	0·71	
Water . , . .	1·56	1·12	1·57	5·8	1·86	1·6	1·40	
	100·00	97·99	100·00	108·3	100·00	99·5 .	99·96	100·00

Peroxide of manganese is prepared by the following processes:—1. Manganoso-manganic or manganic oxide, is boiled with strong nitric acid.—2. Manganous nitrate is gradually heated to incipient redness, and the residue pounded and freed by boiling nitric acid from any remaining manganous oxide; the insoluble residue is then washed and very carefully heated to low redness, stirring all the while (Berthier).—3. Manganous carbonate is heated in an open vessel to 260°, and any portions of carbonate which may then remain undecomposed, are removed by cold and very dilute hydrochloric acid; whereupon, according to Forchhammer, pure peroxide remains behind.—4. Manganous carbonate is carefully heated with fused chlorate of potassium, and the mass, when cold, is well washed with water (Göbel).—5. A solution of a manganous salt, even when very dilute, provided it is perfectly free from iron, deposits peroxide of manganese on the positive pole of a voltaic battery; a feeble current is sufficient for the purpose (Fischer, Kastn. Arch. xvi. 219). Artificially prepared peroxide of manganese is black with submetallic lustre, hard and tough.

Peroxide of manganese, whether natural or artificial, is a good conductor of electricity, and is remarkable for its tendency to become strongly electro-negative in contact with metals, so that powerful voltaic combinations may be made by using a platinum plate covered with it as the negative element. Discs of paper covered with the peroxide are also used in the construction of dry piles. (See ELECTRICITY, ii. 421, 423.)

The peroxide when *heated* alone gives off part of its oxygen, and is reduced to manganic or manganoso-manganic oxide, according to the degree of heat applied; the decomposition takes place more readily in open than in closed vessels (see p. 809). Heated in a charcoal-lined crucible, it is reduced to protoxide, and if mixed with *sulphur*, to manganous oxysulphide, with evolution of sulphurous anhydride. When drenched with strong *sulphuric acid*, it gives off one-fourth of its oxygen and yields a dark red solution of manganic sulphate; and on heating the mixture, another fourth part of the oxygen is given off and manganous sulphate is produced. The reduction is greatly facilitated by mixing the peroxide with organic substances, such as sugar, oxalic acid, &c., carbonic anhydride being then evolved instead of oxygen. With cold *hydrochloric acid* it forms manganic chloride; on heating, manganous chloride, with evolution of chlorine. With *sulphurous acid*, it forms a solution containing manganous sulphate and hyposulphate. By ignition with *potash* in a close vessel, it is resolved into manganous oxide and manganic acid.

The facility with which peroxide of manganese parts with a portion of its oxygen renders it a very valuable oxidising agent, both in the chemical laboratory and in manufactures. It is extensively used for the evolution of chlorine from hydrochloric acid (i. 890), also for discharging the brown and green tints of glass: hence the name *pyrolusite* (from πῦρ fire, and λύειν to wash) applied to the native peroxide, and the somewhat whimsical title, *savon des verriers*, given to it by the French.

Hydrates of the Peroxide.—Peroxide of manganese unites with water in several proportions, according to the mode of preparation.—*α*. In the spontaneous decomposition of manganates or permanganates dissolved in water or in dilute acid, a black-brown hydrated peroxide is precipitated, which cakes together to a black coherent mass containing $MmnO^2.H^2O$ (Mitscherlich). The same hydrate is formed when manganous carbonate suspended in water is treated with chlorine, and the black-brown residue is well washed with dilute acid (Berthier).—*β*. A hydrate containing $2MmnO^2.H^2O$ is obtained when a solution of a manganous salt is precipitated by a mixture of caustic potash and potassic hypochlorite (Winkelblech).—*γ*. The hydrate $3MmnO^2.H^2O$ is deposited on evaporating a solution of manganous bromate (Rammelsberg).—*δ*. $4MmnO^2.H^2O$ is obtained by treating manganoso-manganic hydrate with strong nitric acid (Berthier). See *Gmelin's Handbook*, iii. 206.

According to Görgeu (Ann. Ch. Phys. [3] lxvi. 155; Jahresb. 1862, p. 155) peroxide of manganese acts as an acid, uniting with bases, and reddening litmus slightly when suspended in perfectly pure water; hence Görgeu proposes to call it manganous acid. (See MANGANIC ACIDS, p. 817.)

Oxides of Manganese intermediate in composition between the Sesquioxide and Dioxide.—Under this head are included several ores of manganese, mostly amorphous, one or two of definite constitution, but the greater number merely mixtures of different oxides, which cannot be regarded as definite chemical compounds or distinct mineral species.

a. Psilomelane. $R^2O.Mn^2O^3.H^2O$, with excess of peroxide mechanically combined: the symbol R^2O denotes protoxide of manganese, partly replaced by other protoxides, chiefly baryta and potash. This ore occurs massive and botryoïdal. Hardness = 5 to 6. Specific gravity = 3·7 to 4·328. Lustre submetallic. Streak brownish-black, shining. Colour iron-black, passing into dark steel-grey; opaque. It is a common ore of manganese, occurring frequently in alternate layers with pyrolusite. It is found in botryoïdal and stalactitic shapes in Devonshire and Cornwall, at Ihlefeld in the Hartz, and the other localities undermentioned.

Analyses of Psilomelane.

Locality .	*Schneeberg.*	*Romanèche.*	*Horhausen.*	*Baireuth.*	*Ilmenau.*	*Thiviers.*	*Heidelberg.*	*Ilmenau.*	*Langenberg.*
Analyst .	Turner.		Rammelsberg.	Fuchs.	Scheffler.	Berthier.	Rammelsberg.	Clausbruch.	Heyl.
Manganoso-manganic oxide .	69·80	70·97	81·36	81·8	73·3	64·1	70·17	77·23	68·00
Oxygen . . .	7·36	7·26	9·18	9·5	9·8	7·5	15·16	15·82	13·62
Sesquioxide of iron .	. .	. .	1·43	. .	0·3	6·8			
Protoxide of copper .	. .	. .	0·96	. .	. .	. .	0·30	0·40	0·36
„ cobalt .	. .	. .	. .	. .	. .	. .	0·54		
Alumina . . .	. .	. .	. .	. .	2·1				
Lime	. .	. .	0·38	. .	1·8	. .	0·60	0·91	0·20
Magnesia . . .	. .	. .	0·32	. .	. .	. .	0·21	. .	0·53
Baryta . . .	16·36	16·69	. .	. .	5·8	4·6	8·08	0·12	8·59
Potash . . .	. .	. .	3·04	4·5	. .	. .	2·62	5·29	0·27
Silica	0·26	0·95	0·53	. .	1·7	10·0	0·90	0·52	2·18
Water . . .	6·22	4·13	3·39	4·2	4·3	7·0	1·42	. .	3·95
	100·00	100·00	100·59	100·0	99·1	100·0	100·00	100·29	97·70

β. Varvacite, a mineral from Warwickshire, of crystalline-laminated texture, and specific gravity 4·531 to 4·623, was found by R. Phillips to contain 63 per cent. manganese, 31·6 oxygen, and 5·4 water, agreeing nearly with the formula $Mn^2O.3Mn^2O^3.H^2O$. It is probably an altered manganite consisting largely of pyrolusite.

γ. Wad, Earthy Cobalt, Cupreous Manganese.—These ores occur in amorphous and reniform masses, either earthy or compact, sometimes encrusting or as stains. They are mixtures of different oxides, and not distinct mineral species. Their hardness varies from 0·5 to 6; specific gravity from 3 to 4·26; colour dull black.

Analyses of Wad.

Locality .	*Clausthal.*	*Devonshire.*	*Derbyshire.*	*Vicdessos.*	*Grorel.*	*Siegen.*	*Rübeland.*	*Austerlitz, N. Y.*	*Skidberg.*
Analyst .	Klaproth.	Turner.		Berthier.			Rammelsberg.		Bahr.
Protoxide of manganese	63·3	74·60	34·73	69·8	62·4	58·5	67·50	52·65	61·54
Oxygen . . .	4·7	13·34	3·86	11·7	12·8	10·4	13·48	5·85	4·62
Sesquioxide of iron .	6·5	. .	52·34	. .	6·0	5·7	1·01	22·00	2·70
Protoxide of cobalt .	. .	. .	. .	. .	. .	. .	. .	. .	0·02
Alumina . . .	. .	. .	. .	7·0	. .	10·7	. .	. .	0·75
Baryta . . .	1·0	1·40	5·40	. .	. .	. .	0·36	. .	15·34
Lime	. .	. .	. .	. .	. .	. .	4·22	. .	0·59
Magnesia . . .	. .	. .	. .	. .	. .	. .	. .	. .	0·28
Potash . . .	. .	. .	. .	. .	. .	. .	3·66	. .	0·28
Silica, &c. . . .	8·0	. .	2·74	. .	3·0	1·8	0·47	2·50	0·92
Water . . .	17·5	10·66	10·29	12·4	15·8	12·9	10·30	17·00	12·07
	101·0	100·00	109·36	100·9	100·0	100·0	101·00	100·00	99·11

Analyses of Manganese-ores (continued).

	Cupreous Manganese.				Earthy Cobalt.		
Locality .	*Schlackenberg.*	*Camsdorf.*		*Lauterberg.*	*Oberlausitz.*	*Camsdorf.*	
Analyst .	Kersten.	Rammelsberg.	Böttger.		Klaproth.	Döbereiner.	Rammelsberg.
Protoxide of manganese	66·64	49·99	53·22	27·04	14·4	31·21	40·05
Oxygen. . . .	7·46	8·91	9·14	3·01	1·6	6·78	9·47
Sesquioxide of iron .	0·12	4·70	1·86	29·00	. .	. .	4·56
Protoxide of copper .	4·80	14·67	16·85	11·50	0·2	. .	4·35
Oxide of cobalt . .	. .	0·49	0·14	. .	19·4	32·05	19·45
Alumina . . .	. .	. .	. .	. .	20·4		
Baryta	. .	1·64	1·70	. .	. .	. .	0·50
Lime	. .	2·25	2·85				
Magnesia . . .	. .	0·69					0·37
Potash	. .	0·52	0·65	. .	. .	. .	
Silica, &c. . . .	0·30	2·74	. .	. .	24·8		
Gypsum . . .	1·05						
Water	20·10	14·46	16·94	27·45	17·0	22·90	21·24
	100·47	101·06	103·37	98·00	97·8	92·94	99·99

Wad, or Bog Manganese, consists mainly of oxides of manganese and water, often mixed with silica, alumina, lime, or baryta. *Groroïlite* occurs in roundish masses of brownish-black colour and reddish-brown streak: hardness sometimes 6 to 6·5. It is from Groroi in Mayence, Viedessos in Spain, and Canteen in France.

Cupreous Manganese contains, besides hydrous oxides of manganese, from 14 to 25 per cent. oxide of copper, and 4 to 18 per cent. oxide of cobalt, with various impurities. Specific gravity 3·1 to 3·2. *Pelokonite* is a variety of cupreous manganese, having a liver-brown streak. Hardness = 3. Specific gravity = 2·567.

Earthy Cobalt is a wad in which oxide of cobalt sometimes occurs to the amount of 33 per cent.

Valuation of the Oxides of Manganese.

The numerous applications of the higher oxides of manganese in chemical manufactures, depend upon the quantity of oxygen which they can furnish when exposed to the action of acids, or—what comes to the same thing—the quantity of chlorine which they are capable of eliminating when treated with hydrochloric acid. This will be seen from the following equations, which represent the action of hydrochloric acid on the dioxide, sesquioxide, and red oxide of manganese:

$$\underset{\text{Dioxide.}}{Mn^2O^2} + 4HCl = 2MnCl + 2H^2O + Cl^2$$

$$\underset{\text{Sesquioxide.}}{Mn^4O^3} + 6HCl = 4MnCl + 3H^2O + Cl^2$$

$$\underset{\text{Red oxide.}}{Mn^6O^4} + 8HCl = 6MnCl + 4H^2O + Cl^2.$$

Hence it appears that the quantities of hydrochloric acid required to furnish a given quantity of chlorine, when acted upon by these three oxides, are as the numbers 2 : 3 : 4; or a given weight of hydrochloric acid, acted upon by the three oxides, will yield quantities of chlorine in the inverse ratio of these numbers.

Moreover, as the sesquioxide and red oxide may be regarded (so far as proportional composition is concerned) as compounds of the protoxide and dioxide ($Mn^4O^3 = Mn^2O + Mn^2O^2$; and $Mn^3O^2 = Mn^2O + MnO$), it follows that the commercial value of a manganese-ore may be regarded as proportional to the percentage of dioxide or peroxide contained in it.

The methods of assaying the oxides of manganese may be classed under three heads:—1. The determination of the amount of oxygen disengaged by sulphuric acid.—2. The oxidation of oxalic acid.—3. The evolution of chlorine from hydrochloric acid.

α. The decomposition of peroxide of manganese by *sulphuric acid* takes place as represented by the equation:

$$Mn^2O^2 + H^2SO^4 = Mn^2SO^4 + H^2O + O.$$

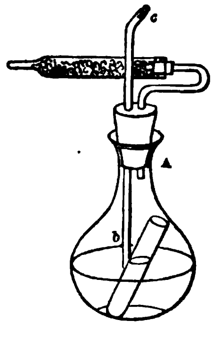
The sample of manganese ore to be tested is heated with strong sulphuric acid in a small retort provided with a bent delivery-tube passing upwards into an inverted bell-jar, filled with and standing in an alkaline liquid, so that any carbonic acid gas that may pass over may be absorbed, and the oxygen alone collected. The contents of the retort are heated to the boiling point, the heat being continued as long as any gas is disengaged. The apparatus is then left to cool, and the volume of gas is measured and corrected for pressure, temperature, and tension of aqueous vapour.

Each atomic proportion (16 pts. by weight) of oxygen evolved corresponds to 1 at. peroxide (87 pts.) in the sample. Moreover, as the reaction is precisely analogous to the decomposition of the peroxide by hydrochloric acid, each at. of oxygen evolved in the one reaction is equivalent to 2 at. chlorine eliminated in the other.

β. By *oxidation of oxalic acid.*—When oxalic acid is heated with peroxide of manganese and hydrochloric acid, the disengaged chlorine converts the oxalic acid into carbonic anhydride, 2 at. carbonic anhydride evolved representing 2 at. chlorine, and therefore 1 at. peroxide of manganese:

$$\underset{\text{Oxalic acid.}}{C^2H^2O^4} + Cl^2 = 2CO^2 + 2HCl.$$

Fig. 731.



The quantity of carbonic anhydride evolved may be determined by means of the flask-apparatus represented in *fig.* 731, and already described under ALKALIMETRY (i. 119). 50 grains of the manganese-ore finely pulverised are introduced into the flask, together with half an ounce of cold water and 100 grains of strong hydrochloric acid in the test-tube; 50 grains of crystallised oxalic acid are then added, the chloride of calcium tube fitted on; the whole quickly weighed; and the process conducted exactly in the same manner as a determination of carbonic anhydride, as described in the article above referred to. The loss of weight of the flask after boiling, gives the quantity of carbonic anhydride evolved, and as 87—the atomic weight of peroxide of manganese—is nearly double that of carbonic anhydride, 44, the loss of weight in the apparatus may be taken approximately to represent the quantity of real peroxide in the 50 grains of the sample. A more exact calculation is easily made.

The quantity of oxalic acid oxidised by a given sample of a manganese-ore may also be estimated volumetrically by means of *permanganate of potassium.* A dilute solution of oxalic acid decomposes permanganates, in presence of sulphuric acid, being itself converted into carbonic anhydride and water, according to the equation:

$$\underset{\text{Permanganic acid.}}{2HMn^2O^4} + 2H^2SO^4 + \underset{\text{Oxalic acid.}}{5C^2H^2O^4} = \underset{\text{Manganous sulphate.}}{2Mn^2SO^4} + 8H^2O + 10CO^2.$$

Under the same circumstances, oxalic acid decomposes peroxide of manganese, atom for atom:

$$Mn^2O^2 + H^2SO^4 + C^2H^2O^4 = Mn^2SO^4 + 2H^2O + 2CO^2.$$

Hence, the amount of peroxide of manganese in an ore may be estimated volumetrically, by allowing it to act upon a known volume of a standard solution of oxalic acid, which is added in excess, and then estimating the amount of undecomposed oxalic acid by a standard solution of permanganate.

The standard solutions required are: 1. *Oxalic acid.*—1 cub. cent. of this solution contains 0·063 grm. of oxalic acid, and corresponds to 0·042 grm. peroxide of manganese. —2. *Permanganate.*—This solution cannot be preserved without decomposition, and is therefore not standardised once for all; but a moderately strong solution is prepared, and its exact value determined before each operation. This is readily done by means of the standard solution of oxalic acid. 5 c. c. of the latter are diluted to 200 c. c.; about 4 c. c. of strong sulphuric acid are added; and the permanganate solution is introduced, drop by drop, from a burette. The dark colour produced by the permanganate disappears slowly at first, but more rapidly as the operation proceeds; the operation is terminated when a faint rose tinge is produced, which remains permanent for a short time. Suppose, for instance, 29 c. c. of the permanganate solution are required: then 1 c. c. of this solution corresponds to $\frac{5}{29} = 0·1724$ c. c. of oxalic acid.

The analysis is conducted as follows:—The ore having been finely powdered and completely dried, 2·1 grms. are treated with about 30 c. c. standard oxalic acid, and 4 c. c. of concentrated sulphuric acid; when the evolution of carbonic anhydride slackens, heat is applied till no more gas is evolved. If any of the ore remains undecomposed, 5 or 10 c. c. more oxalic acid must be added. When the evolution of gas has quite ceased, the clear solution is decanted into a graduated cylinder, and the residue is treated with 2 or 3 c. c. more oxalic acid, and a few drops of sulphuric acid, and again heated. When the decomposition is complete, the solution (residue and all) is washed into the cylinder, and the whole is diluted to a known volume. The mixture thus obtained is never clear; but it need not be filtered, unless it is dark-coloured. A known volume of it is measured off, diluted, acidulated with sulphuric acid, and the amount of non-oxidised oxalic acid is estimated by the permanganate solution, as above; from the result thus obtained, the amount of non-oxidised oxalic acid in the whole mixture is calculated. The number of cubic centimetres of oxalic acid oxidised, multiplied by 2, gives the percentage of peroxide of manganese in the ore. For example, 1 c. c. permanganate solution = 0·1724 oxalic acid. Weight of ore taken = 2·1 grms. Total volume of oxalic used = 48 c. c. The mixture being diluted to 300 c. c., 100 c. c. require 4 c. c. permanganate: hence, the whole 300 c. c. require 12 c. c. permanganate, which correspond to 2·07 c. c. oxalic acid. 48 − 2·07 = 45·93 c. c. oxalic acid, oxidised by peroxide: whence, percentage of peroxide = 45·93 × 2 = 91·86 per cent.

If, instead of 2·1 grms., any arbitrary weight of the ore is taken, the amount of peroxide is calculated by the proportion 100 : 4·2 = number of c. c. oxalic acid used: amount required; the percentage is then calculated as usual.

3. *By the evolution of Chlorine from Hydrochloric acid.*—The ore (the moisture in which is first estimated) is heated in a flask with excess of concentrated hydrochloric acid, and all the chlorine evolved is conducted into a known volume of a standard acid or alkaline arsenious solution, or into excess of iodide of potassium, or into a solution of a known weight of ferrous sulphate, that salt being in excess, and the amount of chlorine is estimated by one of the chlorimetric processes described under CHLORINE, ESTIMATION OF (i. 904). The amount of peroxide of manganese,

corresponding to a given weight of chlorine, is calculated by the proportion $Cl^2 : MmnO^2 = 71 : 87$.

Each c. c. of the acid arsenious solution (i. 904) corresponds to 0·010 grm. chlorine, and to 0·01183, peroxide of manganese; hence 50 c. c. correspond to 0·5 grm. chlorine, and to 0·5915 peroxide. If the ore is rich, about 1 grm. is sufficient for the analysis; if it be poor, from 1·5 to 2 grm. should be taken.

Each c. c. of the alkaline arsenious solution (i. 904) corresponds to 0·00355 grm. chlorine, and to 0·0042 grm. peroxide; hence 100 c. c. correspond to 0·42 grm. peroxide; and if 0·42 grm. be taken for analysis, the number c. c. of arsenious solution which is oxidised by it gives at once the percentage of peroxide. (*Conington's Handbook of Chemical Analysis*, p. 247.)

MANGANESE, OXYCHLORIDE OF. The perchloride of manganese described by Dumas (p. 805) is perhaps an oxychloride.

MANGANESE, OXYSULPHIDE OF. $Mn^2O.Mn^2S$ or $MmnSO$.—This compound is produced when manganous sulphate is ignited in a stream of hydrogen, or, together with sulphide of manganese, when an oxide of manganese is ignited in contact with sulphur. It is a green powder which does not alter at ordinary temperatures, but takes fire when heated, and burns to nearly pure manganoso-manganic oxide, especially if strongly heated at the last. It dissolves in acids as easily as sulphide of manganese prepared in the wet way. (Arfvedson.)

MANGANESE, PHOSPHIDE OF. Obtained by exposing an intimate mixture of 10 pts. of pure ignited dioxide of manganese, 10 pts of white-burnt bones, 5 pts. of white quartz-sand, and 3 pts. of ignited lamp-black for an hour in a closed hessian crucible, to a heat sufficient to melt cast iron; or by strongly igniting 10 pts. of ignited phosphate of manganese, 3 pts. of ignited lamp-black, and 3 pts. of calcined borax in a crucible lined with charcoal. The product is a very brittle, crystalline regulus of the colour of grey cast iron, and of specific gravity 5·951. It is permanent in the air, glows when heated in contact with air, burns with an intense light when heated with nitre. It appears to contain Mn^5P, and is probably a mixture of Mn^3P and Mn^7P, the latter of which compounds is left behind when the substance is treated with hydrochloric acid, while the former dissolves, with evolution of non-spontaneously inflammable phosphoretted hydrogen. (Wöhler, Ann. Ch. Pharm. lxxxvi. 371.)

Schrötter (Jahresb. 1849, p. 247), by heating finely divided manganese in phosphorus-vapour, obtained a phosphide having the composition Mn^6P, of specific gravity 4·94, insoluble in hydrochloric acid, easily soluble in nitric acid.

MANGANESE, SILICIDE OF. The effect attributed to small quantities of silicium in altering the physical properties of metallic manganese has already been mentioned (p. 802). Wöhler (Ann. Ch. Pharm. cvi. 54) has further examined the question by preparing manganese containing larger proportions of silicium. A mixture of about equal parts of fluoride of manganese, water-glass, cryolite, and sodium, pressed into a hessian crucible, and covered with a mixture of chloride of potassium and chloride of sodium, then heated and exposed to a higher temperature, yielded a well fused, hard, brittle regulus containing 11·7 per cent. silicium, exhibiting a somewhat lamino-crystalline structure on the fractured surface, but without visible separation of free silicium; the action of hydrochloric acid upon it was considerably impeded by the separation of oxide of silicium, very dense but not crystalline; the hydrogen gas evolved at the same time contained siliciuretted hydrogen, and deposited amorphous silicium when passed through a red-hot glass tube; hydrofluoric acid dissolved it, with evolution of fetid hydrogen gas. A mixture of fused chloride of manganese and sodium, fluor-spar, water-glass and sodium yielded a well fused, very brittle regulus, containing 13 per cent. silicium, and exhibiting a few cavities filled with steel-grey prismatic crystals. A mixture of fused manganous chloride, fluor-spar, silico-fluoride of potassium, and sodium yielded (after somewhat quicker cooling) a nearly silver-white, very brittle regulus containing 6·5 per cent. silicium and having a conchoïdal strongly shining fracture. A mixture of manganous chloride, sodium, fine quartz-sand and cryolite (the two latter in the proportion of 22 : 26) yielded a yellowish regulus containing 11·4 per cent. silicium, with indications of laminar structure. From these results Wöhler is inclined to believe that even a small quantity of silicium is sufficient to account for the peculiarities of the metallic manganese obtained by Brunner's method.

MANGANESE, RED. Native carbonate of manganese, also called Diallogite (i. 788).

MANGANESE, SULPHIDE OF. *Manganous sulphide*, Mn^2S or $MmnS$, which is the only known sulphide of manganese, occurs native as *Manganese-blende* or *Alabandine*, in the gold mine of Nagyag in Transylvania, sometimes crystallised in cubes and regular octahedrons, with perfect cubic cleavage, but more generally granularly massive. Hardness = 3·5 to 4. Specific gravity = 3·95 to 4·814. It has submetallic lustre and iron-black colour, tarnished brown on exposure. Streak green. Fracture conchoïdal. Before the blowpipe it melts only on the thinnest edges.

The same compound is produced artificially in the dry way, by heating the peroxide with sulphur. Sulphurous anhydride is disengaged and a green powder remains, which dissolves in acids, with evolution of sulphydric acid. The same compound is obtained in the hydrated state by decomposing acetate of manganese with sulphydric acid, or any manganous salt with sulphide of ammonium.

A crystalline sulphide of manganese is obtained by passing the vapour of sulphide of carbon over hydrated manganic oxide ignited in a porcelain tube. The crystals are iron-black rhombic prisms, having a tinge of green and yielding a dingy green powder.

Artificially prepared manganous sulphide soon turns brown by oxidation on exposure to the air. When ignited in the air, it easily gives off all its sulphur as sulphurous anhydride, and leaves manganoso-manganic oxide. Heated in hydrogen gas, it gives off sulphydric acid. It detonates when heated with nitre. Chlorine acts but slowly on it, forming chloride of sulphur. The hydrated sulphide boiled with potash, yields sulphide of potassium and manganous hydrate.

Manganous sulphide dissolves very easily in acids, even in acetic acid; sulphurous acid converts it into hyposulphite with separation of sulphur. When the precipitate is mixed by agitation with neutral metallic solutions, *e. g.* sulphate of cadmium, acetate of lead, ferric chloride, nitrate of silver, sulphate of copper, &c., these metals unite with the sulphur, and the manganese is taken up in their place.

Manganous sulphide forms definite compounds with the sulphides of potassium and sodium.—The *potassium-salt*, $K^2S.3Mn^2S$ or $Mmn^3K^2S^4$, is prepared:—1. By fusing anhydrous manganous sulphate with ⅛ of its weight of lamp-black, and 3 times its weight of carbonate of potassium and sulphur. A gentle heat is applied at first, till the carbonic anhydride is expelled and sulphide of potassium formed; afterwards the heat is raised to bright redness. On cooling, a perfectly fused mass is obtained, which, after the excess of sulphide of potassium has been removed by cold water previously de-aërated by boiling, leaves large dark red scales collected together in masses: these masses may be readily split, like mica, into thin, transparent, dark red laminæ. —2. By substituting peroxide of manganese for the manganous sulphate, a similar compound is obtained, but of less brilliant colour.—The scales, when moist, are rapidly oxidised in the air, becoming black and opaque; but, when perfectly dry, they remain permanent for a considerable time. They are nearly insoluble in water, alcohol, and ether. They detonate violently with nitre. Acids dissolve them, with rapid evolution of sulphydric acid gas. When heated on platinum wire, they become covered with a green powder of oxysulphide of manganese. They are gradually dissolved by water containing air, into sulphate and sulphide of potassium, and manganous hyposulphite, which dissolve, and an insoluble mixture of sulphur and manganic oxide. (Völker, Ann. Ch. Pharm. lix. 35.)

The *sodium-salt*, Mmn^3KS^4, obtained in a similar manner to the potassium compound, forms small, shining, light red needle-shaped crystals, resembling those of sulphide of manganese and potassium in most of their properties, but more readily oxidisable. When treated with distilled water, they rapidly become opaque and dark-coloured. If in this state they are placed over oil of vitriol in a vacuum, they rapidly absorb oxygen as soon as they become moderately dry; and the absorption is attended with so violent a disengagement of heat, that the crystals frequently take fire, and burn like a pyrophorus. (Völker.)

MANGANESE-ALUM. *Manganico-potassic sulphate,* $\left.\begin{matrix}(S\overset{''}{O}{}^2)^2\\ Mmn'''\\ K\end{matrix}\right\}O^4.12H^2O$, found native on the shores of the Great Salt Lake.—A *manganese-magnesium alum* has been found in the Canton Uri in Switzerland. (See SULPHATES.)

MANGANESE-BLENDE. Native manganous sulphide (p. 816).

MANGANESE-GLANCE. Syn. with MANGANESE-BLENDE.

MANGANESE-SPAR. Syn. with DIALLOGITE. Native carbonate of manganese.

MANGANIC ACIDS. Two oxygen-acids of manganese have long been known, viz., manganic acid and permanganic acid, the potassium-salts of which are represented by the formulæ:

Manganate of potassium	$MnKO^3$ or $MmnK^2O^4$
Permanganate of potassium . . .	Mn^2KO^4 or $MmnKO^4$.

Manganic acid cannot exist in the free state; but permanganic acid, $MmnHO^4$, has been obtained as a liquid, and appears to be capable of existing in the solid state. The anhydrides corresponding to these acids, viz., $MmnO^3$ and $MmnO^7$, have not been obtained.

Recent experiments by Gorgeu (Ann. Ch. Phys. [3] lxvi. 153) appear to show that dioxide of manganese, $MmnO^2$, is capable of uniting with alkaline bases, and forming salts which may be called manganites. They appear to have the composition $R^2O.5MmnO^2$ (R denoting a monatomic metal). The potassium-salt is soluble in water; the calcium-salt is a brown precipitate, obtained by adding a solution of manganous nitrate to hypochlorite of calcium.

Manganates. $MnRO^2$, or $MmnR^2O^4$.—These salts are isomorphous with the sulphates, selenates, and chromates. Only three of them have, however, been obtained, viz., the barium-, potassium-, and calcium-salts. They have a green colour, but are very unstable, especially in solution, being quickly converted into permanganates, with separation of manganic oxide: the decomposition is accelerated by the presence of acids, and retarded by alkalis.

Manganate of Barium. $MnBaO^2$, or $MmnBbaO^4$.—This salt is obtained by igniting peroxide of manganese with nitrate of barium, or better, by adding the peroxide in fine powder, and by small portions, to a mixture of hydrate of barium and chlorate of potassium, heated to fusion, and afterwards dissolving out the chloride of potassium by water. It is a green powder, insoluble in water. It may, however, be obtained in the crystalline state by mixing a solution of permanganate of barium with baryta-water, and leaving the liquid to stand in a loosely-covered vessel. (Mitscherlich.)

Manganate of Potassium. $MmnK^2O^4$.—When dioxide of manganese is strongly ignited with hydrate or carbonate of potassium in excess, manganic acid is formed, under the influence of the alkali, together with a lower oxide of manganese. Ignition in open vessels, or with an admixture of nitrate of potassium, increases the production of the acid, by the absorption of oxygen which then occurs. The product has long been known as *mineral chameleon*, from the property of its solution, which is green at first, to pass rapidly through several shades of colour. A more convenient process for preparing manganate of potassium is that recommended by Dr. Gregory. He mixes intimately 4 pts. of dioxide of manganese in fine powder with 3½ pts. of chlorate of potassium, and adds the mixture to 5 pts. of hydrate of potassium dissolved in a small quantity of water. The mixture is evaporated to dryness, powdered, and afterwards ignited in a platinum crucible, but not fused, at a low red heat. The ignited mass, digested in a small quantity of cold water, forms a deep green solution of the alkaline manganate, which may be obtained in crystals of the same colour by evaporating the solution over sulphuric acid in a vacuum.

Manganate of potassium is not soluble in water without decomposition. When water is poured upon the crystals, they are resolved into permanganate of potassium, and a black crystalline compound of potash with peroxide of manganese (manganite of potassium) which almost immediately gives up its potash to the water, and leaves pure hydrated peroxide of manganese. (Mitscherlich.)

$$\underset{\text{Manganate.}}{3MmnK^2O^4} + 2H^2O = \underset{\text{Permanganate.}}{2MmnKO^4} + 4KHO + MmnO^2.$$

According to Gorgeu (*loc. cit.*), when carbonic anhydride is passed through a solution of potassic manganate till the alkali is completely converted into carbonate, permanganate of potassium is formed, together with a yellow hydrated precipitate containing *manganite of potassium*, $K^2O.5MmnO^2$, or $Mmn^5K^2O^{11}$.

Manganate of potassium dissolves without decomposition in water containing free alkali. If potash be added, not in too great excess, but still sufficient to form a green solution, this solution sometimes turns red when warmed, and remains so after cooling; but if briskly stirred, it turns green again.

When a very strong solution of potassic manganate is exposed to the air till the potash has absorbed carbonic acid, crystals are sometimes formed consisting, according to Mitscherlich, of *acid manganate of potassium*, $MmnKHO^4$.

Manganate of Sodium.—Obtained by igniting peroxide of manganese with caustic soda. It is so very soluble in water, that it cannot be obtained in the crystalline state (Mitscherlich). According to Gentele, however (J. p. Chem. lxxxii. 58), manganate of sodium is obtained in nearly colourless crystals resembling Glauber's salt, and containing $MmnNa^2O^4.10H^2O$, by heating equal parts of finely-pulverised peroxide of manganese and nitrate of sodium in a muffle to a bright red heat for 16 hours, boiling the pulverised black mass with water, and leaving the solution to stand in a cold place. The crystals dissolve in water with slight decomposition, yielding a green solution. According to Wöhler (Ann. Ch. Pharm. cxix. 375), on the other hand, this process does not yield a trace of sodic manganate, because the nitrate of sodium is decomposed before the temperature required for the formation of the manganate it attained; in fact, the decomposition is so complete, that the process might be used for the preparation of pure hydrate of sodium. [But why does not this hydrate of sodium act on the peroxide of manganese so as to form sodic manganate and a lower oxide?]

Permanganates. Mn^2RO^4, or $MmnRO^4$.—These salts are more stable than the manganates, and are, in fact, produced by their oxidation. They are isomorphous with the perchlorates, $ClRO^4$; a fact which affords a strong argument in favour of the diatomicity of manganese, inasmuch as if the metal be regarded as monatomic, the formulæ of the permanganates and perchlorates do not exactly correspond, the one containing 2 at. Mn, whereas the other contains only 1 at. Cl.

Permanganate of Ammonium. $Mmn(NH^4)O^4$.—When permanganate of silver is triturated with an equivalent quantity of sal-ammoniac and with water, a purple-red solution is formed, which, when decanted from separated chloride of silver, yields by evaporation, crystals corresponding in composition with the above formula, and not containing any water of crystallisation. They are trimetric, and similar in form to the potassium-salt, but with somewhat different angles: $a : b : c = 0{\cdot}8050 : 1 : 0{\cdot}6519$. $\infty P : \infty P = 77° 40'$; $\breve{P}\infty : \breve{P}\infty = 78° 0'$. When dried by heat, they quickly decompose.

Permanganate of Barium. Mn^2BaO^4, or Mmn^2BbaO^8.—This salt may be prepared by passing carbonic anhydride through water in which impure manganate of barium, obtained by calcining peroxide of manganese with nitrate of barium, is suspended, till the salt is completely decomposed, then decanting, boiling for a while in order to decompose the resulting acid carbonate of barium, and evaporating the clear solution to the crystallising point. Or permanganate of silver is decomposed by an equivalent quantity of chloride of barium dissolved in water, and the solution is evaporated.

Permanganate of barium forms black prisms, permanent in the air, and isomorphous with anhydrous sulphate and selenate of sodium (Mitscherlich). When the red solution of this salt is mixed with baryta-water, it aquires a violet colour, loses after a while its alkaline reaction, and yields by evaporation crystals of manganate of barium.

The permanganates of *calcium*, *copper*, *magnesium*, *sodium*, *strontium*, and *zinc* are prepared like the ammonium-salt: they are deliquescent and difficult to crystallise. The *lithium-salt* crystallises more readily.

Permanganate of Hydrogen, or Permanganic acid. $MmnHO^4$.—This acid may be obtained in the state of aqueous solution, by decomposing the barium-salt with sulphuric acid. As thus obtained by Mitscherlich, the free acid appeared to be a body not more stable than peroxide of hydrogen, being decomposed between 30° and 40°, with escape of oxygen gas and precipitation of hydrated peroxide of manganese. It bleached powerfully, and was rapidly destroyed by all kinds of organic matter. Hünefeld, on the other hand, obtained permanganic acid in a state in which it could be preserved, evaporated, redissolved, &c. He washed the manganate of barium with hot water, by which it is resolved into dioxide of manganese and permanganate of barium, and then added to it the quantity of phosphoric acid exactly necessary to neutralise the baryta. The liberated permanganic acid was dissolved out, evaporated to dryness, and by a second solution and evaporation, obtained in the form of a reddish-brown mass, crystalline and radiated, which exhibited the lustre of indigo at some points and was entirely soluble in water. When the dry permanganic acid was fused in a retort with anhydrous sulphuric acid, and afterwards distilled at a higher temperature, an acicular sublimate of a crimson red colour was obtained, which appeared to be a combination of permanganic and sulphuric acids. (Berzelius' *Traité*, i. 522.) When monohydrated sulphuric acid is poured upon a somewhat considerable quantity of crystallised permanganate of potassium, the salt is decomposed, with great evolution of heat, red flames bursting out, oxygen being given off, and manganic oxide being set free in dark-brown flakes and shreds like spider-lines. The red flames seem to show that permanganic acid is gaseous at the high temperature produced by the reaction. Its volatility has been further demonstrated by Terreil (Bull. Soc. Chim. de Paris, 1862, p. 40), who makes use of this property to obtain the acid in the pure state. For this purpose, permanganate of potassium is dissolved in sulphuric acid (H^2SO^4) diluted with 1 at. water; and the greenish-yellow solution is distilled over the water-bath at 60° or 70°. The apparatus then becomes filled with violet vapours, which condense to a soluble greenish-black liquid, not containing either chlorine or sulphuric acid, but consisting of pure permanganic acid. It is difficult, however, to prepare a large quantity of the acid at once in this manner, inasmuch as, at a certain moment, as soon as the quantity of the distillate has become somewhat considerable, it decomposes spontaneously, with slight detonation and separation of manganic oxide.

Permanganic acid thus obtained is a thick, greenish-black, metallic-shining liquid, which appears to be capable of solidifying. It greedily attracts moisture; its solution has a violet colour, and, if protected from dust, may, when dilute, be preserved with tolerable facility. When quickly heated, it detonates; but if slowly warmed, it volatilises in violet vapours, having a peculiar metallic odour. It possesses very great oxidising power, instantly setting fire to paper and alcohol, the latter with explosion. In contact with fatty bodies, it detonates with violence. When a few drops of aqueous sulphite of potassium are let fall on permanganic acid, a very brisk reaction takes place; part of the acid is carried forward in vapours, and the vapours decompose as they diffuse through the air, depositing a shower of brown flocks. Permanganic acid dissolves to a certain extent with green colour in strong sulphuric acid. The solution in acid containing 3 at. water, is violet; a difference which seems to indicate the existence of an anhydrous and a hydrated permanganic acid. (Terreil.)

Permanganate of Lead, Mmn^2PpbO^4, is formed, on mixing a solution of nitrate of lead with permanganate of potassium, as a brown precipitate, soluble without residue in nitric acid.

Permanganate of Potassium. $MmnKO^4$.—This salt may be prepared by the following processes:—1. One pt. of peroxide of manganese is ignited with 1 pt. of hydrate of potassium (or 1·8 of nitre); the resulting mass dissolved in water; and the red solution decanted and evaporated, rapidly at first till small needles appear, afterwards cautiously, so that the crystallisation may go on regularly (Chevillot and Edwards).—2. Chlorate of potassium being kept in a state of fusion over a spirit-lamp, hydrate of potassium is first added to it, and then an excess of finely-divided peroxide of manganese, which immediately dissolves, forming a splendid green solution. The mixture is then heated till the whole of the chlorate is decomposed; and the mass, when cold, is boiled with a small quantity of water, whereupon the green colour of the solution changes to red; finally, the liquid is decanted from the peroxide of manganese while still hot, and set aside to crystallise by cooling (Wöhler, Pogg. Ann. xxvi. 626). Gregory (J. Pharm. xxi. 312) adds a solution of 10 pts. (3 at.) of hydrate of potassium in a very small quantity of water to a finely-divided mixture of 8 pts. (3 at.) of peroxide of manganese and 7 pts. (1 at.) of chlorate of potassium; evaporates to dryness, during which a small quantity of mineral chameleon is formed; ignites the finely powdered mass in a platinum crucible over a spirit-lamp, till the whole of the chlorate of potassium is decomposed (for which a low red heat is quite sufficient); reduces the semi-fused mass to coarse powder; boils it in a larger quantity of water; allows the insoluble portion to subside, and decants; evaporates the clear solution rapidly; again decants from the freshly precipitated peroxide of manganese; and leaves the solution to crystallise by cooling. The crystals are then washed with a small quantity of cold water; dissolved in the smallest possible quantity of boiling water; and the solution is left to crystallise by cooling. In this manner needles are obtained three-quarters of an inch in length, and amounting in weight to about a third of the peroxide of manganese employed. If it be desired to filter the solution, in order to avoid the loss arising from decantation, a funnel may be used, having its neck filled with asbestos.

The salt crystallises in dark purple-red needles, having first a sweet, and afterwards a rough taste; it does not redden turmeric, and is permanent in the air. The crystals are trimetric; $a : b : c = 0·79523 : 1 : 0·6478$; $\infty P : \infty P = 76° 59'$; $\breve{P}\infty : \breve{P}\infty = 78° 20'$. They are prismatic, exhibiting the combination $\infty P . \breve{P}\infty$, the latter often predominant; frequently, also, with oP and other faces. The salt dissolves in 16 pts. water at 15°.

The crystals decrepitate when *heated*, evolve 10·8 per cent. of oxygen gas, and are converted into a black powder from which water extracts manganate of potassium, leaving 54 per cent. of black manganic oxide. When heated in an atmosphere of *hydrogen gas*, they become red-hot and diminish in bulk, at first rapidly, afterwards slowly, with formation of a green mixture of hydrate of potassium and protoxide of manganese. The salt, when triturated with *sulphur*, produces a series of small detonations. Mixed with an equal weight of sulphur and heated to 177°, it explodes with flame. *Phosphorus* produces a much louder detonation when triturated with it, also when heated with it to 70°. *Charcoal, arsenic,* and *antimony* likewise take fire when heated with the salt.

A solution of permanganate of potassium containing *perchlorate*, deposits crystals containing the two salts in the same proportion as the solution. In presence of a very large excess of perchlorate, they are red; but if the proportion of permanganate amounts to one half, they appear black.

Permanganate of Silver, $MmnAgO^4$, is obtained, according to Mitscherlich, on mixing warm solutions of nitrate of silver and permanganate of potassium, the solution as it cools depositing the salt in large regular crystals, which require 190 times their weight of water at 15° to dissolve them. In warm water they are much more soluble, but they cannot sustain a boiling heat without decomposition.

The manganates and permanganates, especially the latter, are used as oxidising agents for a variety of purposes. A solution of permanganate of potassium is quickly deoxidised, and consequently decolorised, by sulphurous acid, by neutral solutions of sulphides and pentathionates, and by acid solutions of sulphites, hyposulphites, tetrathionates, sulphocyanates and nitrites; more slowly by trithionates. Acidulated solutions of mercurous, ferrous, stannous and antimonious salts, and acid solutions of arsenious acid, likewise rapidly decolorise a solution of a permanganate. A solution of permanganate of potassium constitutes a test-liquid of great use in volumetric analysis, as we have already had occasion to notice (see i. 263; ii. 59; iii. 384).

The manganates and permanganates likewise act very rapidly on organic matter, and may therefore be employed as disinfecting agents. Solutions of these salts have, in fact, lately been prepared on the large scale for this purpose by Mr. Condy. Putrid water from stagnant pools is rapidly deodorised by these solutions. Their freedom from odour and perfectly innocuous character render them available for many purposes for which other disinfectants cannot be used, as for application to wounds and fœtid sores: they may also be advantageously used for the purification of tainted provisions. On the other hand, their fixed character renders them less adapted for purifying infected atmospheres than the hypochlorites, which evolve a gas capable of acting on the organic matter in the air. (See Hofmann's *Report on Chemical Products and Processes in the International Exhibition of* 1862.)

MANGANITE. Native manganic hydrate (p. 810).

MANGIFERA GABONENSIS. The tree which yields the so-called Dika bread (ii. 330).

MANGOLD WURZEL. See Beta (i. 582). On the changes which take place in the composition of the plant during its growth, see R. Hoffmann. (Bull. Soc. Chim. de Paris, 1864, p. 393.)

MANGOSTIN. $C^{20}H^{22}O^{5}$. (W. Schmid, Ann. Ch. Pharm. xciii. 83).—A substance contained in the husk of the fruit of *Garcinia Mangostana* (ii. 771). To obtain it, the dry husks are boiled with water to extract tannin, then treated with hot alcohol, and the alcoholic extract is left to evaporate, whereupon it deposits mangostin as a yellow crystalline substance, mixed with a large quantity of yellow amorphous resin. To remove the latter, the whole is dissolved in alcohol, and the solution is mixed with sufficient water to render it opalescent; it then, on cooling, deposits, first the resin, afterwards the mangostin in small yellow laminæ. For further purification, the alcoholic solution is precipitated with basic acetate of lead; the washed precipitate is suspended in water, and decomposed by sulphydric acid; the filtrate is mixed at the boiling heat with water, till it becomes milky; and the mangostin which separates from it on cooling is finally purified by crystallising it several times from dilute alcohol.

Mangostin thus prepared forms thin golden-yellow laminæ, destitute of taste and smell. It melts at about 190°, without loss of water, to a dark-yellow liquid, which solidifies to an amorphous mass; by a stronger heat, the greater part of it is decomposed, the remainder subliming unaltered. It is insoluble in *water*, but dissolves easily in *alcohol* and in *ether*, forming neutral solutions. Warm *dilute acids* dissolve it without alteration; by heating with strong *nitric acid*, it is converted into oxalic acid. *Alkalis* dissolve it with yellow or brownish colour. It reduces the *noble metals* from their solutions: with *ferric chloride*, it forms a dark greenish-black solution, the colour of which disappears on the addition of acids. It is not precipitated by any metallic salt, excepting *basic acetate of lead*. The yellow precipitate thrown down from the alcoholic solution by neutral acetate of lead and a little ammonia, gave by analysis (at 100°), in one experiment, numbers agreeing nearly with the formula $4C^{20}H^{22}O^{5}.5Pb^{2}O$.

MANIHOTIC ACID. An acid said to have been obtained from the root of *Jatropha Manihot*; it crystallises in prisms, having an acid taste, and forms, with baryta, lime, and magnesia, neutral, easily fusible salts, crystallising in nodules; but its existence is not well established. (Handw. d. Chem. v. 113.)

MANILA GUM. A resin of unknown origin, resembling Copal and Dammara resin. It dissolves for the most part in alcohol of 90 per cent., and melts easily, diffusing an odour like that of the resin of the Coniferæ. (Buchner.)

MANIOC. The Indian name of the nutritious matter of *Jatropha Manihot*, from which cassava and tapioca are made in the West Indies. It has been analysed by Payen. (Compt. rend. xliv. 401.)

MANNA. A saccharine juice which exudes from certain species of ash and other plants. It has a strong smell, a sweetish, slightly nauseous taste, and acts as a mild purgative, but is also more or less nutritious.

The trees which yield the manna of commerce are two species of ash growing in the warmer parts of Europe and in the East, viz., *Fraxinus Ornus*, Linn., which grows in the South of Europe, in mountainous situations, especially in Calabria and Sicily; and

Fraxinus rotundifolia, Lamarck, or *Ornus rotundifolia*, Persoon—the round-leaved, flowering, or manna ash, which grows in Calabria and in the East. According to Decandolle, it is from this latter tree that manna is chiefly obtained. The manna flows naturally from the trees, and attaches itself to their sides in the form of white transparent drops; but the extraction of the juice is facilitated by incisions made during summer.

The finest kind of manna is called **flake manna** (*Manna cannulata* vel *canellata*). It is white or yellowish-white, light, porous and friable, the fractured surface exhibiting a number of small capillary crystals. Its odour somewhat resembles that of honey; its taste is sweet, but afterwards rather acrid.

Inferior sorts are: 1. The *Sicilian manna*, which is the commonest in English commerce, consisting of small, soft, round fragments of a dirty yellowish-brown colour, intermixed with particles of dark flake-manna: this kind contains many impurities. —2. *Manna in sorts* (*in sortis*), which may be subdivided into: a. *Gerace*, which approaches most nearly to flake manna; and, β. *Capace*, which comprises not only that from the district so called, but also that of Cinesi and Faberetti in Sicily; it is fatty, sticky, and hard, though clearer in appearance than the last.—3. *Manna calabrina*, which stands between the last two (a and β), but is now of rare occurrence in commerce.—4. An inferior kind, known as *Manna communis*, is found in the Neapolitan province of Capitanata, on the declivities of Mount St. Angelo. It is not fatty, but very damp, and is chiefly consumed in Italy, and sent to the Levant. The yearly production of this kind of manna amounts to more than 200 tons.

Analyses of Manna.

According to **Buchols**.*	
Mannite	60·0
Fermentable but uncrystallisable sugar, with colouring matter (purgative bitter matter?)	5·5
Sweetish gum	1·5
Gummy extractive	0·8
Fibro-glutinous matter	0·2
Water and loss	30·0
	98·0

According to **Leuchtweiss**.†	*M. cannellata.*	*M. cannel. in fragmentis.*	*M. calabr.*
Mannite	42·6	37·6	32·0
Sugar	9·1	10·3	15·0
Mucilage, with some mannite, resinous and acid matter, and a small quantity of nitrogenous substance	40·0	40·8	42·1
Insoluble matter	0·4	0·9	3·2
Water	11·6	13·0	11·1
Ash	1·3	1·9	1·9
	105·0	104·5	105·3

There are also several varieties of saccharine exudations, known under the name of manna, not produced by the ash. Of these Landerer enumerates eight, viz.: 1. *Manna laricina*, from the leaves of *Larix europæa;* also called Briançon manna. According to Berthelot, it contains melezitose (*q. v.*).—2. *Manna cedrina*, from the branches of *Pinus cedrus*. This variety is brought from Mount Lebanon, and has great repute in Syria.—3. *M. celastrina*.—4. *M. quercina*.—5. *M. australis*, produced by *Eucalyptus resinifera*.—6. *M. cistina* s. *labdanifera*, a rare variety met with in Greece. This is derived from several species of *Cistus*, and is called Cistus manna.—7. *M. Althagnia*, the exudation of *Hedysarum Alkago*, a plant indigenous in Arabia, and growing also in the maritime districts of Greece. This manna is supposed to exude from the *Hedysarum*, which covers extensive plains in Arabia and Palestine, as a result of the wounds produced on the plants by the browsing of sheep and goats. It is used as nutriment by the Arabs, as well as by those who form the caravans which cross the Desert. According to Landerer, it is this variety, and not the produce of the ash, which corresponds to the *mel ex aëre* of Pliny, and the *humor melleus* of Theophrastus.—8. *Manna tamariscina*, called also *Manna Israëlitarum*, and believed by Landerer to be the manna mentioned in the Old Testament. He informs us that this exudation is produced by the puncture of *Coccus manniferus*, an insect inhabiting the trees of *Tamarix mannifera*, which grow abundantly in the neighbourhood of Mount Sinai. The manna exudes as a thick transparent syrup, covering the smaller branches, from which it flows. It is collected by the monks of the district in the month of August. The collection takes place very early in the morning, at which time, owing to the coolness of the night, the saccharine juice has become to some extent congealed. The tamarisk manna is eaten in Palestine, and in the district of Sinai, as a delicacy, and is said to be efficacious in diseases of the chest. It is soluble in water and alcohol, and the aqueous solution readily undergoes fermentation. The alcohol which it yields has a peculiar odour, resembling that from the fruit of *Ceratonia siliqua*, which contains butyric acid. The manna must therefore contain fermentable sugar, in place of mannite [or together with the latter]. (*Pereira's Materia Medica*, 4th ed. vol. ii. [1] p. 673.) According to Berthelot (Compt. rend. liii. 583), the tamarisk manna from Sinai contains 55 per cent. cane-sugar, 25 inverted sugar (ii. 863), and 20 dextrin, &c.; manna from Kurdistan contains 61 per cent. cane-sugar, 15·6 inverted sugar, and 22·5 dextrin, &c.

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* Jahrb. pr. Pharm. lxi. (1809).

† Ann. Ch. Pharm. liii. 124.

MANNIDE.
MANNITAN. } See the next article, p. 825.

MANNITE. *Sugar of Manna. Sugar of Mushrooms.* $C^6H^{14}O^6$.—This substance was discovered by Proust (Journal f. Chem. u. Phys. v. Gehlen, ii. 83), and has been investigated by many chemists, including, among others, Liebig, Frémy, Strecker, Berthelot, Wanklyn, Erlenmeyer, and Linnemann. (For references, see *Gmelin's Handbook*, xv. 356.)

The following plants and parts of plants contain mannite ready formed: the roots of *Aconitum Napellus*; of celery, from *Apium graveolens*; of *Meum athamanticum*; of *Œnanthe crocata*; of *Polypodium vulgare*; of *Scorzonera Hispanica*; the root-bark of *Tunica Granatum* [constituting Latour's *Granatin*]; the roots of *Triticum repens*. The bark of *Canella alba* contains about 8 per cent. of mannite; that of *Fraxinus excelsior* contains mannite. The leaves and young twigs of *Syringa vulgaris* contain mannite [which, mixed with *Lilacin*, constitutes Bernays' *Syringin*: also, the leaves of *Ligustrum vulgare*; celery-leaves; the foliage of *Cocos nucifera*; the fruit of *Laurus Persea*, of *Cactus opuntia*. Coffee-beans contain mannite, according to Döbereiner. Ergot of one year contained mannite, that of another year mycose. Many *fungi* contain mannite. On *algæ* there is often found an efflorescence of mannite, which, according to Stenhouse, may also be obtained from the dry algæ; according to Phipson, mannite does not exist in fresh algæ, but is formed from vegetable mucilage by fermentation. It is formed very abundantly during the viscous fermentation of sugar, and to a greater or less extent during fermentation generally. In the transformation of starch into glucose by boiling with dilute sulphuric acid, it is also formed as a secondary product. Finally, Linnemann (Ann. Ch. Pharm. cxxiii. 136) has obtained it by the action of sodium-amalgam on glucose.

Mannite is usually prepared from manna, which is treated with boiling alcohol, and the alcoholic solution allowed to crystallise. On cooling, mannite is deposited. It is purified by recrystallisation, and appears to be very easily obtainable in a high state of purity.

Mannite crystallises in thin four-sided prisms, which sometimes grow to a considerable size. One of the characteristics of mannite is the ease with which it may be crystallised from its solution in water or in alcohol. The crystals contain no water of crystallisation, and are but very slightly hygroscopic.

At 18°, 1 pt. of mannite dissolves in 6½ pts. of *water*. At 15°, 1 pt. of mannite dissolves in 80 pts. of *alcohol* (specific gravity 0·898), and in 1,400 pts. of absolute alcohol. In boiling alcohol, it is much more soluble. In *ether*, it does not dissolve at all.

An aqueous solution of mannite does not become syrupy on being spontaneously evaporated; in this respect it differs strikingly from a solution of sugar. It is only slightly sweet to the taste. It does not exert any action on polarised light.

Mannite differs from sugar in its power of resistance to the action of heat. It melts between 160° and 165°; at about 200° it begins to boil, and may be distilled with very little decomposition, even at the ordinary atmospheric pressure. In sealed tubes it will bear a heat of 250° without suffering much decomposition; at higher temperatures it carbonises.

It does not ferment except under very unusual conditions. It does not reduce oxide of copper to the state of suboxide; but hinders the precipitation of sulphate of copper by the fixed alkalis, causing the formation of a beautiful blue-purple solution instead. It may be boiled with solution of potash without imparting a brown colour to the solution.

The composition of mannite was determined some years ago by Liebig, who fixed upon the formula which is at present admitted; but, as was shown a short time ago (Proceed. Roy. Soc. Edinburgh, 1861–62; Ann. Ch. Pharm. cxxiii. 372; Chem. Soc. J., xvi. 221), this must have been by accident; for, until quite recently, nothing was known about mannite which could lead to the adoption of one rather than another of three or four formulæ, each of them equally probable.

The close analogy subsisting between mannite and glycerin was shown by Berthelot (*Chimie organique fondée sur la Synthèse*, par M. Berthelot), who obtained a great variety of salts of mannite by heating a mixture of mannite with different acids to a temperature of between 200° and 250°: nitro-mannite, which is really the nitrate of the series, had been previously discovered by Flores Domonte and Menard (1847), and then investigated by Strecker.

The connection between mannite and the hexylic group was shown by Wanklyn and Erlenmeyer in 1861, by the conversion of mannite into iodide of hexyl, by means of hydriodic acid:

$$\underset{\text{Mannite.}}{C^6H^8(HO)^6} + 11HI = C^6H^{13}I + 6H^2O + 5I^2.$$

By this transformation the formula of mannite, which up to that time was doubtful, was fixed with certainty.

The chemical character of mannite is that of a polyatomic alcohol: it is a hex-atomic alcohol:

$$\left.\begin{matrix}(C^6H^8)^{vi}\\ H^6\end{matrix}\right\}O^6 : \text{type} = \left.\begin{matrix}H^6\\ H^6\end{matrix}\right\}O^6.$$

Or, it may be regarded as hydride of hexyl in which 6 atoms of peroxide of hydrogen replace 6 atoms of hydrogen:

$$C^6H^8(HO)^6 : \text{type}, C^6H^{14}.$$

It is closely related to the sugars, glucose becoming mannite when acted upon by nascent hydrogen, whether that hydrogen be a product of fermentation or of the action of sodium-amalgam on water:

$$\underset{\text{Glucose.}}{C^6H^{12}O^6} + H^2 = \underset{\text{Mannite.}}{C^6H^{14}O^6}.$$

Glucose is probably derived from the hydrocarbon C^6H^{12}, being $C^6H^6(HO)^6$.

On being heated to a temperature of 200°, mannite loses water and passes into mannitan (Berthelot):

$$C^6H^{14}O^6 - H^2O = C^6H^{12}O^5.$$

This conversion seems to be partial. Mannite is likewise converted into mannitan by prolonged boiling with strong hydrochloric acid.

When mannite is oxidised with *nitric acid*, it is converted into saccharic acid, and not into mucic acid: on pushing the oxidation further, oxalic acid is obtained.

Fusion with *caustic potash* causes disengagement of hydrogen, and production of formate, acetate, and propionate of potassium. Distilled with *lime*, it appears to give acetone.

With *fuming nitric acid*, or better with a mixture of *nitric* and *sulphuric acids*, it gives nitro-mannite, $C^6H^8(NO^3)^6$.

With *sulphuric acid* it gives a coupled acid, sulpho-mannitic acid:

$$(C^6H^8)^{vi}H^3O^6.(SO^2)^3H^3O^3.$$

Heated for some hours to a little over 200° with organic acids, it forms salts which bear a considerable resemblance to the fats. (Berthelot.)

When it is heated with *bromide of ethyl* and potash, it furnishes ethyl-mannite.

According to Berthelot, when it is kept for several weeks in contact with *water*, *chalk* and *cheese*, or other protein-compound, at a temperature of 40°, it gives rise to alcohol, carbonic, lactic, butyric and acetic acids, and hydrogen: at the same time there is no production of yeast, and no fat, nor glycerine nor sugar. If a slit testicle be employed as a ferment, then there is production of sugar.

Inasmuch as glycerin has been produced artificially from a derivative of propylene, viz., from $C^3H^5Br^3$, there is reason to expect that mannite will be made from a derivative of hexylene. Up to the present time, however, the synthesis of mannite has not been realised.

Salts of Mannite.—In Berthelot's *Chemie organique, &c.*, a number of organic salts of mannite are described, *i. e.*, acetate, butyrate and dibutyrate, palmitate, stearate, oleate, benzoate, and tribenzoate. They are prepared in general by heating mannite or mannitan with the acid to a temperature ranging between 200° and 250° for from 12 to 15 hours. At the end of this process more or less of the salt is found. In order to purify the salt, the crude product is treated with excess of an alkali (baryta or carbonate of sodium) which combines with the acid that has not been used up by the mannite or mannitan, but does not attack the organic salt which has been produced. Ether is then added and dissolves the salt. The ethereal solution, on being evaporated, yields the salt, which is an oil or a fat according to acid employed.

Of the salts above mentioned the butyrate appears to be the easiest to prepare; but in all cases only a portion of the mannite or mannitan undergoes conversion into a salt. There is the closest resemblance, both physically and chemically, between the salts of glycerin and these salts of mannite.

Berthelot regards these salts as derivatives, not of mannite, $C^6H^{14}O^6$, but of mannitan, $C^6H^{12}O^5$. Their formulæ (given under ETHERS, ii. 521) require confirmation.

Derivatives of Mannite.

Mannide. $C^6H^{10}O^4 = C^6H^{14}O^6 - 2H^2O$.—Discovered by Berthelot, who obtained it by acting upon mannite with butyric acid. It constitutes a syrup, which is at first sweet to the taste, and afterwards bitter. It is very soluble in water and in absolute alcohol, even in the cold.

A remarkable circumstance connected with it is its volatility. It is sensibly volatile at 100°, and evaporates rapidly at 140°.

It is highly deliquescent, passing gradually into mannite when it is exposed to a moist atmosphere. Exposed in an open vessel to the air in the usual state, it absorbs as much as 40 per cent. of moisture, whilst in air saturated with moisture, it will sometimes take up as much as 80 per cent.

Mannide is not an ether, but a derivative of the hydrocarbon C^6H^{10}, viz., $C^6H^6(HO)^4$.

Mannitan. $C^6H^{12}O^5$.—Discovered by Berthelot. Obtained, but only in small quantity, by heating mannite to about 200°. A better method of preparation is by the long-continued boiling of mannite with strong hydrochloric acid; or by the saponification of a salt of mannite. It is a curious fact, that the salts of mannite always give mannitan on saponification, the mannitan passing subsequently more or less completely into mannite.

Mannitan is a syrup with a slightly sweetish taste. It may be very readily distinguished from mannite by its solubility in absolute alcohol, which thus affords a means of effecting a separation of these two substances. It is very soluble in water, but insoluble in ether.

On being exposed for a length of time to the atmosphere, it undergoes a very partial conversion into mannite. Boiling with alkalis or dilute acids accelerates this change.

When heated above 140°, it partly volatilises.

With respect to its rational constitution, it appears to the writer of this article that mannitan is not an ether of mannite. It would seem rather to be derived from a lower hydrocarbon:

Mannite being derived from C^6H^{14}, *i. e.*, $C^6H^8(HO)^6$.
Mannitan „ from C^6H^{12}, *i. e.*, $C^6H^7(HO)^5$.

The ease with which hexylic compounds pass into hexylene is again encountered in the mannite compounds, which are hexyl-compounds that have suffered replacement of hydrogen by peroxide of hydrogen. (See HEXYL-COMPOUNDS.)

Nitro-mannite. $C^6H^8(NO^3)^6$.—Prepared by treating mannite with the strongest nitric acid and sulphuric acid. It forms beautiful fine white acicular crystals, insoluble in water, but soluble in alcohol or ether. It explodes very violently on being struck with a hard substance. If carefully heated, it may be decomposed without explosion; but when it is suddenly heated, it explodes, but not with great violence. It seems to suffer spontaneous decomposition on being kept for a long time.

It has been proposed to use nitro-mannite for charging percussion-caps, but apparently without success.

A reaction of nitro-mannite which is of considerable theoretical interest is that with sulphide of ammonium, by which reagent it is converted, not into a nitrogenous organic base, but into mannite.

Sulpho-mannitic acid ($C^6H^{14}O^6 3SO^3$). A kind of mannite-sulphovinic acid, is formed by the action of strong sulphuric acid upon mannite. A barium-salt, $C^6H^{11}Ba^3O^6 3SO^3$, and other salts of this acid, have been obtained. J. A. W.

MANNITIC ACID. $C^6H^{12}O^7$.—An acid produced, together with mannitose, by the oxidation of mannite under the influence of platinum-black; it was first observed by Döbereiner, and more completely investigated by Gorup-Besanez (Ann. Ch. Pharm. cxviii. 257). To prepare it, mannite is mixed with twice its weight of platinum-black; and the mixture, moistened with water, is exposed to a temperature not exceeding 30° or 40° at the utmost, as long as it contains any undecomposed mannite (about three weeks for 20 or 30 grains of mannite). The mass is then exhausted with water; the solution precipitated with basic acetate of lead; the well-washed precipitate decomposed by sulphydric acid; and the solution is evaporated, first over the water-bath, then in the cold over sulphuric acid.

Mannitic acid is not crystallisable, but forms a gummy mass, soluble in water and in alcohol, nearly insoluble in ether. It reduces cuprous oxide from an alkaline cupric solution, and throws down metallic silver from the nitrate.

The mannitates have not yet been obtained in the crystalline form. The composition of the salts analysed by Gorup-Besanez corresponds with the formula $C^6H^{10}M^2O^7$. The *calcium-salt*, $C^6H^{10}Ca^2O^7$, is precipitated from its aqueous solution by alcohol. The *copper-salt*, $C^6H^{10}Cu^2O^7$, remains as a green amorphous mass when its aqueous solution is evaporated. The *lead-salt*, $C^6H^{10}Pb^2O^7$, separates on cooling from the solution obtained by boiling mannitic acid with lead-oxide. The *silver-salt*, $C^6H^{10}Ag^2O^7$, separates as a greenish-yellow precipitate on mixing a concentrated solution of the calcium-salt with nitrate of silver.

MANNITOSE. $C^6H^{12}O^6$.—A kind of sugar, isomeric with glucose, produced, together with mannitic acid, in the oxidation of mannite under the influence of platinum-black (Gorup-Besanez, *loc. cit.*). It is fermentable, but does not act on polarised light. It exhibits, with alkalis, alkaline cupric solutions, basic nitrate of bismuth, carbonate of sodium, and other reagents, the same behaviour as dextro-glucose (ii. 860), but does not unite with chloride of sodium; its alcoholic solution mixed with alcoholic potash containing 11·27 per cent. potash, forms a semifluid yellow precipitate, corresponding with the formula $K^2O.2C^6H^{12}O^6$. (Gmelin's *Handbook*, xv. 339.)

MANURE. *Dünger. Engrais.*—This term, in its widest signification, is applicable to any material used in agriculture and horticulture for the purpose, and with the effect, of accelerating vegetation, or of increasing the production of cultivated plants. In a usual and more limited sense, it signifies the accumulated refuse of the dwellings, stables, and cattle-yards of a farm—including animal excreta, decaying remains of plants, &c. (See Voelcker, 1856–9, *Journal of the Royal Agricultural Society of England*, xvii. 191; xviii. 111; xix. 112; xx. 134; On the Composition of Farm-yard Manure.—Lawes, 1862 *ibid.* xxiii. 45.) Burnt lime, marl, clay, gypsum, &c. are also commonly used as manure.

In addition to these kinds of manure which are produced upon the farm as the result of its internal economy, or obtained in the immediate neighbourhood of the land to which they are applied, a variety of other materials are employed for the same purpose, under the name of *artificial manure*. These materials are chiefly obtained by the farmer from extraneous sources, and sometimes from considerable distances, according to their value. They comprise guano (ii. 952), bones (i. 619), prepared phosphatic minerals (APATITE, i. 348; COPROLITES, i. 82), ammonia-salts, nitrates, the refuse of slaughter-houses and of various manufactures; fish, sea-weed, &c.; the refuse of towns, in the form either of night-soil or sewage; and artificial saline mixtures. (See Ure's *Dictionary of Arts, Manufactures, and Mines*, iii. 36 *et seq.*; also Way 1849, *Journ. Roy. Agric. Soc. Eng.* x. 196—Composition and Value of Guano, 1851, *Ib.* xii. 204—On Superphosphate of Lime, 1856, *Ib.* xvi. 533—Value of Artificial Manures.—Voelcker, 1861–2, *Ibid.* xxi. 350; xxiii. 277—Chemical Composition and Commercial value of Phosphatic Manures and Artificial Manures.)

The fertilising influence of manure is a fact which has been established by universal experience wherever the cultivation of plants has been practised. In agriculture—considered as that branch of industry which is concerned in the manufacture of food for man and domesticated animals, and therefore the most important art of civilised life—manure may be regarded as being, to a great extent, the raw material employed. A complete knowledge of the causes to which the efficacy of manure is due, and of the mode in which it acts, would comprise the whole chemistry of agriculture. The right management of the manure naturally resulting from systematic agriculture is the basis on which rests the profitable practice of the art, the fundamental principle which should regulate all the operations of the farm, and determine all their details. It is only by means of such knowledge that it can be possible to modify and improve the method of culture, or to make a right selection and use of other materials, besides the natural manure of the farm, with the object of augmenting, artificially, the produce of land, by rendering effective, in a higher degree, the natural sources of fertility.

The principles involved in the action of manure are to some extent deducible from that knowledge of the general phenomena of vegetation which has been acquired chiefly within the present century, and has begun to assume consistency and system only within the last five-and-twenty years. The data upon which that knowledge is founded were contributed chiefly by the successive researches of Priestley, Ingenhousz, Sennebier, Woodhouse, Saussure, and Davy. But though they afforded materials for a view of the chemistry of vegetation, more correct than that which considered decaying animal and vegetable substances as the chief food of plants, they were but little regarded; and though the researches of Saussure were conducted with special reference to agricultural practice, still the humus theory of plant-nutrition held its ground, and was adopted by Davy in his lectures on the "Elements of Agricultural Chemistry," delivered before the Board of Agriculture between 1802 and 1812. In those lectures he did little more than state the general problem to be solved in the application of chemistry to agriculture, and insist upon the important relation between the science and the art; but they afford some remarkable illustrations of the correct appreciation of natural facts which was characteristic of his genius. (Priestley, 1772, *Phil. Trans.* 72; lxii. 157–200.—Ingenhousz, 1779, *Experiments on Vegetables, &c.*; 1782, *Phil. Trans.*; 1784, Sur l'Economie de Végétaux, *Jour. Phys.* xxiv.; 1798, *Essay on the Food of Plants and the Renovation of Soils.*—**Hassenfratz**, 1792, *Jour. Phys.* xiii., xiv. Sur la Nutrition des Végétaux.—**Kirwan**, 1794, *Trans. Roy. Irish Acad.* v. 123. What are the manures most advantageously applicable to various sorts of soils, and what are the causes of the beneficial effect in particular instances?—**Sennebier**, 1800, *Physiologie végétale, &c.*—**Woodhouse**, 1802, *Nicholson's Journ.*—**Saussure**, 1804, *Recherches chimiques sur la Végétation.*—**Davy**, *Collected Works*, vii., viii.)

Following in the track of **Saussure's** researches, **Boussingault** entered upon the study of the same subject, conducting his experiments on a much larger scale, and with a more direct relation to agricultural practice than had hitherto been attempted. In this country, **Lawes** was also led, by the suggestive work of **Saussure**, to study the effects of various earthy and saline substances upon the growth of different plants, and the researches of both have been continued to the present time. **Boussingault's** first memoirs on the subject were published in 1836, and in the year 1839 he had made known results of his investigations, which—besides establishing the composition of the most important kinds of agricultural produce; the efficacy of various materials in feeding animals, and the general relations between the composition of the crops obtained and the manure used in the ordinary routine of practice in his locality—had led him to adopt the conclusions, that the carbon and nitrogen obtained in the several crops comprised in a rotation, amounted to much more than was contained in the manure supplied within the same time; and consequently, that those constituents must be derived in some way from the atmosphere during vegetation; that those alternations of crops which admitted of accumulations of carbon and nitrogen being gathered from the atmosphere, and conserved upon the farm most largely, in the form of manure, were the most advantageous; that certain plants were better fitted for this purpose than others; and that the value of manure was, to a great extent, indicated by the amount of ammonia or nitrogen which it contained. (See **Boussingault**, 1836, *Ann. Chim. Phys.*; Recherches sur la quantité d'Azote contenu dans les Fourrages, et sur leur Equivalens, lxiii. 225-244, 1838, lxvii. 408-421; Examen comparatif des Circonstances météorologiques sous lesquelles végètent certaines Plantes alimentaires, à l'équateur et sous la zône tempéré, *ib.* 337-358; 1837, Des Influences météorologiques sur la Culture de la Vigne, lxiv. 174; Mémoire sur la quantité de Gluten contenue dans les Farines de plusieurs espèces de Froment cultivées dans le même sol, lxv. 301; De la Discussion de la valeur relative des Assolements par l'analyse élémentaire, *Compt. rend.* vii. 1149; viii. 54.)

Ingenhousz and **Saussure** had already adopted the opinion that the carbon of plants was, to a great extent, derived from the atmospheric carbonic acid; and the same view had been put forward by **Brongniart**, in reference to the origin of the coal strata, as more probable than the humus theory. (**Brongniart**, 1837, *Compt. rend.*, Considérations sur la Nature des Végétaux qui ont couvert la surface de la Terre aux diverses époques de sa formation, v. 403-415.)

But it was not until the year 1840 that a comprehensive theory of plant-nutrition was propounded by **Liebig**, with such perspicuity and force as to excite universal attention. The fundamental proposition of that theory was, that the food of plants, the materials from which the chief mass of their substance is produced in vegetation, consists solely of carbonic acid, water, and ammonia. The chemical arguments by which this view was supported, in opposition to the prevailing opinion, that plants derived their carbon, hydrogen, oxygen, and nitrogen from humus, and from other vegetable and animal substances, were conducted in such a convincing and logical manner, that Liebig has been generally regarded as being entitled to the same honour in the establishment of this theory of plant-nutrition, as if the data on which it was based had altogether originated with himself. Liebig's researches on the phenomena of the decay of animal and vegetable materials afforded, together with the existing knowledge of the phenomena of animal life, the most conclusive evidence that the ultimate products of those processes were carbonic acid, water, and ammonia, precisely those materials constituting the chief food of plants. Moreover, these substances cannot be combined, in any way, so as not to contain a far greater amount of oxygen than the substances of which plants collectively consist, and which are produced in vegetation. This fact showed that elimination of oxygen was a necessary feature of vegetation, and threw an entirely new light upon the known constitution of the atmosphere and the decomposition of carbonic acid by growing plants; at once establishing a most remarkable relation between the phenomena of vegetation and of animal respiration, and demonstrating the essential interdependence of the processes of animal and vegetable life.

From the fact that the food of animals is provided exclusively by the vegetable kingdom, either directly, in the form of corn, roots, fruit, &c.; or indirectly, through the medium of animal life, as the flesh of herbivorous animals, the importance of a knowledge of the chemistry of vegetation, in reference to the cultivation of plants as a source of food for animals, is self-evident. Consequently, **Liebig's** exposition of his theory of plant-nutrition had especial reference to the practice of agriculture, just as the researches of Saussure, Boussingault, Lawes, and others, had been prosecuted in the same direction; and it was developed, in its application, into a theory of agriculture. (Liebig, 1840, *Chemistry in its Applications to Agriculture and Physiology.*)

In order to illustrate fully the chemistry of manures, and the principles involved in their use, as well as in the general routine of agricultural practice, it will be necessary to give a brief statement of the general features of the chemistry of vegetation, considered from an abstract point of view, so far as the present knowledge of that subject will permit; then to describe the conditions which exercise the chief determining influence upon vegetation, in regard to the object appertaining to agriculture generally, and the different means adopted for the attainment of that object, according to the modification it receives by the various special circumstances under which the art is practised.

The ultimate result of the growth and development of plants consists in the production of a number of oxygenated and nitrogenous hydrocarbon compounds:—starch, sugar (ii. 856), gum (ii. 953), lignin (i. 818), fat (ii. 616), albumin (i. 69), gluten (ii. 873), legumin (iii. 568), fibrin (ii. 643), &c., which, in some form of subordinate modification, are universal constituents of all plants; and a great variety of other analogous substances, which are special constituents of particular plants or of particular plant-organs.

The chief mass of the solid portion of plants consists of these substances; it is the main function of vegetation to produce them, and thus to provide food for animals. (See Nutrition.)

These constituents of plants were formerly termed, in a chemical sense, "organic" substances, in conformity with the opinion that they could be produced only by the plant-organism, under the influence of vital action; and that they were totally distinct, in their chemical nature, from the compounds producible artificially, and from those belonging to the mineral kingdom, which were termed "inorganic" to distinguish them chemically from the proximate constituents of organised bodies—either plants or animals—and from the derivatives of those compounds. Modern chemistry, however, has discarded that opinion, and with it the use of the terms organic and inorganic, as expressive of a distinction which no longer represents a recognised difference; but the term "organic" is still conveniently applied to the constituents of plants and animals without involving such a distinction. (Gerhardt, 1853, *Traité de Chimie organique*, i. 1–6.)

The materials from which the proximate constituents of plants are produced in vegetation are few. According to the present state of knowledge, carbonic acid is the principal source of the carbon; but in the case of some plants, a further portion of carbon may possibly be derived from other carbon-compounds. (See Humus, iii. 76, and Ulmin.) Water is the source of hydrogen and oxygen, while nitrogen is derived chiefly from ammonia; to some extent also from nitric acid; possibly from nitrogenous substances analogous to humus, and from the elementary nitrogen of the atmosphere; but whether directly or indirectly, or even at all, has not been ascertained. The preponderance of evidence is in favour of the opinion that elementary nitrogen is not directly assimilated by plants. See on this subject: Saussure, 1804, *Recherches* &c.—Davy, *Collected Works*, vii., viii.;—Boussingault, 1838, *Ann. Chim. Phys.* lxvii. 1–54, lxix. 353–367; Recherches chimiques sur la Végétation, entreprises dans le but d'examiner si les Plantes prennent de l'azote à l'atmosphère, 1854 [3] xli. 1–60; 1855, xliii. 149–223; 1856, xlii. 1–41; 1858, *Compt. rend.* xlvii. 807; 1838, *Compt. rend.* vi. 129; 1839, vii. 889.—Liebig, 1840, *Chemistry, &c.*—Mulder, 1845, *The Chemistry of Vegetable and Animal Physiology.*—G. Ville, 1853, *Recherches expér. sur la Végétation*; 1856, *Compt. rend.* xlii. 679; xliii. 85, 143, 612.—Mène, 1851, *Compt. rend.* xxxii. 180, 770.—Roy, 1854, *Compt. rend.* xxxix. 1133.—Cloez and Gratiolet, 1850–5, *Compt. rend.* xli. 775, 935.—De Luca, 1856, *Compt. rend.* xliii. 865.—Harting, 1855, *Compt. rend.* xli. 942.—Petzholdt, *J. pr. Chem.* lxv. 101–105.—Lawes, Gilbert, and Pugh, 1862, On the Sources of Nitrogen in Vegetation, *Phil. Trans.* for 1861, p. 431 *et seq.* and, 1863, *Journ. Chem. Soc.* (2) I. 100.—Lehmann, *Physiological Chemistry*, Cavendish Soc. iii. 178.—Mohl, *The Vegetable Cell*, by Henfrey, pp. 77–88.

Among the substances above named, carbonic acid, water, and ammonia constitute the chief materials of plant-food; and since it is from them that the organic constituents of plants are principally produced in vegetation, they have been sometimes called the "organic materials of plant-food" (*Quarterly Review*, lxix. 336; Schleiden, *The Plant*, p. 173). Under natural conditions, these substances are constantly supplied to plants by the atmosphere (i. 437–439), which contains them in small proportion, but in large aggregate quantity, continually replenished by the process of animal life (see Respiration); by the decay of dead animals and plants (Eremacausis, ii. 497); by several natural phenomena of the mineral kingdom (i. 770, ii. 835); by industrial and economic operations (Combustion, i. 1095; Fuel, ii. 722); by rain, dew, and the evaporation of water from the ocean, lakes, and rivers (see Water and Ammonia, i. 182). It is immaterial whether these substances are supplied to plants exclusively by the atmosphere, or whether they are derived from other sources as well; in either case their value in regard to vegetation is the same. They may, therefore, be termed collectively the air-food of plants; and the organic substances produced from them in vegetation may be designated the air-derived constituents of plants. So far as relates to the merely abstract view of the chemistry of vegetation, it is a matter of indifference whether the materials, constituting the air-food of plants, are derived exclusively and directly from the atmosphere, or whether they are to some extent derived from other sources also, and indirectly; as, for instance, by the decay of humus or nitrogenous animal or vegetable substances contained in the soil, or supplied to it as manure. The case is different, however, when vegetation is regarded from a practical point of view—as the means of producing food for animals artificially—and when the objects and circumstances of the practice of agriculture have to be included in the consideration of that subject, the difference is of the highest importance.

But there are also other materials concerned in vegetation besides the carbonic acid, water, ammonia, &c., from which the plant constructs its chief substance. In almost all plants, and in every organ of a plant, there are certain substances—indestructible by fire—which remain as ashes when plants are perfectly burnt. (See Ash, i. 416 *et seq.*)

The ash of all plants contains potash, soda, lime, magnesia, phosphoric acid, sulphuric acid, silica, iron, &c., which, in the case of land-plants, are derived exclusively from the soil on which the plants grow. The relative proportions of these substances vary considerably in different plants, and in the different organs of the same plant; sometimes also, though in a less degree, according to the character of the soil on which the plant grows; but most of them are, in greater or less amount, constant constituents of plants, and are therefore to be regarded as necessary to their existence and essential to vegetation. (See Kirwan, 1794, *op. cit.* 145, 148— Saussure, 1804, *Recherches chimiques sur la Végetation*, pp. 261, 269.)

In connection with the chemistry of agriculture, these substances have been commonly called the "mineral" or the "inorganic" constituents of plants; mineral,[*] in accordance with the recognised classification of natural objects, into mineral, vegetable, and animal, because they are earthy in their nature, and are likewise derived from the earth; inorganic, to distinguish them from the organic constituents of plants, which are produced in vegetation from carbonic acid, water, and ammonia. (H. Davy, *Elements of Agricultural Chemistry*, 1827, Collected Works, viii. 40, *et. seq.*; Liebig, *Chemistry in its applications to Agriculture and Physiology*, 1840, p. 92, *et seq.*)

The condition in which the above substances are found in the ashes of plants is doubtless very different from that in which they exist in the plants themselves, and very little is known as to what that may be. The functions they perform in vegetation are also little understood. The amount of them contained in plants is comparatively very small; but those which are constant and essential constituents of particular plants being necessary to vegetation, must be regarded as indispensable constituents of plant-food. (See Kirwan, *op. cit.* 149, 157—Saussure, *op. cit.* p. 261.) This is evident from the fact that plants will not grow to maturity under conditions which exclude a supply of the ash-constituents found in them under ordinary circumstances. The necessity of the ash-constituents in vegetation is rendered still further apparent by the fact that the fluids and organs of animals contain precisely those ash-constituents which are always found in fully-developed plants. (BILE, i. 587; BLOOD, i. 609; BONE, i. 619; CHYLE, i. 961; FLESH, ii. 663; GASTRIC JUICE, ii. 822; MUSCULAR TISSUE; NERVOUS TISSUE.)

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[*] This use of the epithet "mineral" to denote those constituents of plants which are not dissipated by fire, as well as to distinguish them from the other constituents, and from other materials of plant-food—carbonic acid, water, and ammonia—has recently been objected to by a high chemical authority, as an error in nomenclature, indicating confusion of ideas, since the epithet "mineral" applies "equally to *all* the elements, both volatile and fixed, of plant-food" (Hofmann, *Chemical Products and Processes—International Exhibition*, 1862, Class II. Section A, *Reports by the Juries*, p. 159). Since the chemistry of agriculture is a subject concerning which it is especially desirable that any real or supposed confusion, whether of terms, or of ideas, or of facts, should be stringently eradicated, and kept clear of, I shall, in submission to that authority, abstain from such use of the term "mineral," substituting for it the term "ash," to denote those constituents of plants which, being earthy, are derived exclusively from the soil; and shall follow the same rule in reference to the materials of plant-food which are supplied exclusively by the soil, in order to distinguish them from the other materials of plant-food—carbonic acid, water, and ammonia. In doing so, however, I may remark that the use of the term "mineral," which is now condemned, has long been common among chemists; and will venture to suggest that there is no reason, beyond obedience to authority, for abstaining from that use of the term which has been customary. For though the epithet "mineral" unquestionably does apply "equally to *all* the elements, both volatile and fixed, of plant-food," still it does so only in a Natural History sense, not as synonymous with the chemical term "inorganic," when used in its true sense as the antithesis to "organic." Nor has the use of the term "mineral," in special reference to the chemistry of agriculture, been such as to indicate its equivalence to, or confusion with, the term "inorganic," when used in its true chemical sense. On the contrary, the term "mineral" has been used in reference to that subject, during the last fifty years at least, for the specific designation of the ash-constituents of plants; and during the last thirty years, to distinguish those substances from the other "inorganic" materials of plant-food—carbonic acid, water, and ammonia. This is aptly illustrated in "*An Address to the Agriculturists of Great Britain, explaining the Principles and Use of Artificial Manures*, by Professor Justus Liebig—Liverpool, 1845, p. 8—by the description, "They are mineral substances, and as such, are indestructible by fire; and, consequently, remain as ashes after the incineration of the plants, or of their parts." (See also Schleiden, *The Plant*, p. 173.) In fact, the term "mineral," so used, has a real advantage, in being more precise than the term "inorganic," also used, in some instances, by Liebig and others, for the special designation of the fixed, ash, or soil-constituents, as contradistinguished from the other materials of plant-food—carbonic acid, water, and ammonia—which, in a chemical sense, are also "inorganic," but which have frequently been called the "organic" materials of plant-food (See Liebig, 1840, *Chemistry in its Applications to Agriculture and Physiology*, pp. 3, 92, 114.—Boussingault, 1845, *Rural Economy*, p. 490.—*Quarterly Review*, 1842, lxix. 336, *et seq.*—Lawes and Gilbert, 1847—64. *Journ. Roy. Agricult. Soc.* viii. xii. xvi. xvii. xviii. xxi. xiii. &c.—B. H. P.

Moreover, the functions of these ash-constituents in the process of animal life, have been so far traced, that there cannot be any doubt of their being essential to it, both in the growth of animals—when they partly remain in the body, contributing to its increase—and during the life of mature animals, when they no longer remain and accumulate in the body, but are eliminated, either directly or indirectly, in common with the rest of the daily food, in the excretions, after having performed their quota in the chemical process of animal life. (See NUTRITION.)

The ash-constituents of plants have, therefore, a two-fold importance, being essentially concerned both in vegetation and in animal life. Since they cannot be derived from the atmosphere, it is evident that the soil on which plants grow has a far more important share in vegetation than that of affording merely mechanical support: that it is likewise the source of an essential portion of their food. (See *ante*, p. 829.)

The mode in which the materials of plant-food are taken up into the organism of the plant is twofold: partly by means of the leaves, and partly by the roots. The absorption of carbonic acid by the leaves and green parts of plants, first observed by Priestley (1772, *Phil. Trans.* lxii. 166), and more fully demonstrated by Saussure and Sennebier, is one means by which plants may appropriate carbon, and perhaps water; but whether they obtain nitrogen in the same way, has not been proved (see Mohl, *The Vegetable Cell*, p. 86). The ash-constituents of plants can be introduced into their organism only by the roots, and the structure of plants justifies the opinion that they are taken up in the state of solution in water (Mohl, *op. cit.* p. 65). But, besides the ash-constituents, other food-materials are taken up by the roots, especially in cultivated plants—carbonic acid, ammonia, or other nitrogenous substances, resulting from the decomposition of humus, and perhaps also carbonaceous compounds other than carbonic acid. (See Mohl, *op. cit.* pp. 80, 81.—Mulder, *The Chemistry of Vegetable and Animal Physiology*, pp. 142–188.—Trinchinetti, *Sul Facoltà assorbente della Radici*, pp. 55.—Boussingault, *Rural Economy*, p. 41 *et seq.*)

Scarcely anything is known as to the precise influence exercised upon the growth and development of plants by the relative amounts of air-food supplied by the atmosphere and from within the soil, or of the modifications of growth which may result from such influences; though there are numerous facts, established by agricultural experience, which apparently indicate that this circumstance is in some cases of especial importance in determining the character of the produce. (See pp. 841, 844.)

Nor are the special functions of particular materials of plant-food in the growth of plants any better understood, though experience appears to indicate that they are useful in some other way than by directly contributing to the increase of mass in the plant; and it is far from being established that either the kind or amount of the substances of which plants consist afford a quantitative indication of the food-materials which are necessary in their growth. This is especially the case with cultivated plants which are frequently grown with special objects, requiring a disproportionate development of particular organs and constituents.

These circumstances render it very doubtful whether the requirements of plants during their growth, can be correctly measured by a knowledge of their composition alone, any more than it would be possible, in the case of animals, to determine the quantities of food required during their existence, merely from a knowledge of the qualitative and quantitative composition of the animal at any period of its life.

The various materials concerned in vegetation as plant-food, are all equally necessary for the growth and development of the great majority of plants. No one of them can be replaced by anything else, not even by an increased amount of some other of them. All must be supplied together; in the absence of any one, the rest, however abundant, are wholly incapable of supporting vegetation, and deficiency of any one limits the effect of the remainder.

However, the relative proportions of the several materials of plant-food requisite for vegetation, are not absolutely constant for all plants: on the contrary, they vary to some extent for different plants, or families of plants: some plants drawing more largely upon the air-food than others; some requiring a greater proportion of ash-constituents, Among the former, some produce the nitrogenous constituents in larger proportion than others; while some produce chiefly the corresponding non-nitrogenous constituents. Among the latter, some require alkalis, some phosphoric acid in preponderating amount, others require chiefly lime, silica, &c.

The special conditions under which plants grow also exercise a considerable influence in modifying their requirements as regards the several food-materials, and in determining the size of particular organs, as well as the relative proportion of the nitrogenous and non-nitrogenous constituents produced. Many plants become, under cultivation, totally different, both in structure and composition, from what they are in a state of natural vegetation; but the extent to which this influence is, or may be exerted, is far from being sufficiently known, nor are the conditions which determine it fully ascertained. Climate and season, the physical condition of the soil, the greater or less facility with which some or all of the food-materials may be obtainable by plants in particular cases, and the copious or scanty supply of certain food-materials, are all doubtless influential in this respect, and this subject still offers a wide field for observation and research.

Among those conditions of vegetation which are neither chemical nor climatic, the physical characters and state of land exercise great influence upon the amount of produce. Soils differ naturally, in this respect, according to the relative proportions of clay, sand, gravel, &c., which they contain, and they differ, perhaps still more widely, in regard to the texture they possess, or are capable of acquiring by tillage. (See SOILS, and Boussingault, 1845, *Rural Economy*, pp. 258–308.)

The essentially chemical conditions of vegetation consist then, in a supply of food-materials: they comprise the existence in the soil of the requisite ash-constituents in a state fit for assimilation by plants, and a supply of the requisite air-food. Wherever these conditions obtain in due proportion, together with the conditions of climate, &c., required by particular plants—whether perennial or annual—those plants will grow, attain maturity, and perfect development.

So far then as relates to the purely chemical conditions of vegetation, other conditions being the same, the quantity of plant-substance produced within a given time on a given area of land—the amount of produce—will be determined, within certain limits, by the quantity of plant-food supplied; and it will be limited by the available quantity of that constituent of the food which is supplied meanwhile, in least amount, relatively to the general requirements of the particular plant growing.

Since the very striking differences recognisable in vegetation at different places, or on different land, and manifested in the unequal amount of produce, cannot be ascribed to the atmospheric supply of air-food, which is always constant, and everywhere the same, it becomes necessary to seek in the soil for the chemical cause of these differences in the degree of fertility as represented by the amount of produce. The soil being the only source of the ash-constituents of plant-food, the capability of performing its share in the chemical conditions of vegetation must necessarily depend upon its containing the requisite ash-constituents, in sufficient amount, and in such a state, as to be available in the growth of plants.

When it is considered that soils have been formed by the mechanical and chemical alteration of rocks possessing the most varied composition, that they consist of the disintegrated débris of granite, basalt, clay-slate, limestone, sandstone, chalk, &c., it is evident that their chemical constituents must vary very considerably according to the particular rocks from which they have originated, just in the same manner as they differ in being sandy, calcareous, loamy, or argillaceous.

The total amount of the ash-constituents concerned in vegetation will therefore be very different in different soils. Moreover, the different chemical nature of the minerals constituting the rocks from which soils have originated, and the unequal susceptibility of those minerals to decomposition under atmospheric influences, give rise to wide differences between soils in regard to the chemical condition the ash-constituents they contain. Both these circumstances may influence the fertility of land.

The mechanical operations of tillage, besides communicating to soils that texture which is necessary to admit of the free development of the roots, are also conducive to the chemical alteration of minerals in the land, by facilitating the access of atmospheric air, and the consequent decomposition of insoluble alkaline silicates. The fertilising influence of tillage upon land, especially when it contains a large proportion of clay, has long been known, and it was at one time believed to be a substitute for manuring. Tull, *Horse-hoeing Husbandry*.—Smith, *A Word in Season: Lois Weedon Husbandry*.

The analysis of soils, from which so much advantage was at one time anticipated, has not been found so useful as had been supposed in regard to agriculture, or, indeed, capable of affording any trustworthy indication as to the composition of soils or their defects; but the following statement of the most prominent features of a number of analyses of soils, made by several chemists under the direction of Magnus, will serve to give some idea of the variation affecting the most important constituents, phosphoric acid and potash, &c., existing in such states as to be soluble and insoluble in dilute hydrochloric acid. (**Magnus**, 1846, *Ann. der Landwirthschaft*, xiv. 2: Bericht über Versuche betreffend die Erschöpfung des Bodens, welche das Königliche Landes Oekonomie-Kollegium veranlasst hat.)

	Percentage amount of ash-constituents in soils.					Quantity per acre at a depth of one foot. Soluble in acid. Average.
	Soluble in dilute acid.			Insoluble in acid.		
	Average.	Maximum.	Minimum.	Maximum.	Minimum.	
Lime . . .	0·895	. .	. .	. .	. .	35,794 lbs.
Magnesia . .	0·260	. .	. .	. .	. .	10,180
Potash . .	0·221	0·530	trace	3·406	trace	8,983
Soda . . .	0·161					
Silica . . .	0·448	. .	. .	. .	. .	17,920
Phosphoric acid .	0·172	0·651	trace	. .	. .	7,581
Sulphuric acid .	0·154					
Ammonia . .	. .	. .	. .	. .	. .	8·4

The extent of the resources of land in ash-constituents is still further illustrated by the following table calculated from the results of experiments conducted by **Lawes** and **Gilbert** at Rothamsted, in which wheat was grown every year on the same land without any manure for 20 years. The land was a heavy loam, resting upon chalk. The average amount of produce in the neighbourhood at the time when the experiments were commenced was under 22 bushels per acre, and wheat was grown only once in five years. When the experiments were commenced in 1843, the land was in such a condition that, according to the ordinary routine, it required to be again manured with farm-yard manure: for since the previous application of manure, four crops had been removed from it, viz. barley, peas, wheat, oats. See **Lawes** and **Gilbert**—1847—*op. cit.* viii.—Agricultural Chemistry—1864—*Ibid.* xxv.—Report of Experiments on the Growth of Wheat—1857—*Chem. Soc. Qu. J.* x. 1.—On some Points in the Composition of Wheat Grain; its Products in the Mill and Bread.)

	Ash-constituents removed from land by wheat.					
	In 20 consecutive years.			In average annual crop.		
	Total produce.	Corn.	Straw.	Total produce.	Corn.	Straw.
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Total ash-constituents .	2241·00	354·00	1887·00	112·00	18·00	94·00
Silica	1229·77	3·54	1226·23	61·48	0·18	61·30
Phosphoric acid . .	252·56	177·10	75·46	12·62	8·85	3·77
Potash . . .	360·94	106·26	254·68	18·04	5·31	12·73
Soda	9·43	. .	9·43	0·47	. .	0·47
Lime	105·49	11·16	94·33	5·28	0·56	4·72
Magnesia . . .	77·40	39·67	37·73	3·87	1·98	1·89
Sulphuric acid . .	51·88	. .	51·88	2·59	. .	2·59
Chlorine . . .	37·73	. .	37·73	1·89	. .	1·89

The soils in which the fertilising effects of tillage are most marked, are generally of a clayey nature, and are therefore capable of furnishing a larger supply of ash-constituents under the influence of atmospheric decomposition. But there is another characteristic which such soils possess in a high degree, viz., the capability of absorbing ammonia from the atmosphere. (See **Faraday**—1825—*Quarterly Journ. of Science*, xix. 16 *et seq.*) By reason of this capability, they store up, during the period of fallow, the ammonia conveyed to them from the atmosphere by rain and otherwise, and thus provide an increased supply of this air-food to plants requiring it. (See **Lawes** and **Gilbert**, *Op. cit.* xvii. 293 *et seq.*)

The absorptive power of soils is not limited to ammonia, but extends likewise to most of the important ash-constituents of plant-food which are soluble in water. This fact was first observed by **Thompson** (1850, *Journ. Roy. Agric. Soc. of England*, xi. 68), and was afterwards investigated by **Way** (*Ibid.* xi. 313.; xiii. 123). It is highly probable that the condition in which substances are thus retained by soils, so as to be gradually supplied to the roots of plants by the medium of carbonic acid and water, is of great importance in regard to the nutrition of plants, and to the relative fertility of land. (See SOILS; Way and Voelcker, *Op. cit.*; Liebig, *The Natural Laws of Husbandry*, p. 66 *et seq.*)

In considering the chemical conditions which determine the relative fertility of land, it will be convenient to examine, in the first place, how far this is determined by the ash-constituents. So far as these alone are concerned, the degree of fertility of land —its capability of contributing to the growth of a greater or less amount of produce— would be, in a strictly chemical sense, proportionate to the available amount of ash-constituents it was capable of furnishing within the period of growth; but the amount of produce would not vary in the same ratio, because the ash-constituents of land cannot be useful in vegetation, except in so far as they can co-operate with a due proportion of air-food.

If the sources of air-food, available during the period of growth, were limited to the constant atmospheric supply, the amount of produce would be proportionate to the capability of assimilation by the plant, under the other prevailing conditions of climate, season, &c.

But if other sources of air-food were available within the period of growth, in addition to the atmospheric supply, and together with an abundant supply of ash-constituents by the land, the amount of produce would be largely augmented under conditions otherwise the same.

Thus plants growing upon land affording only a scanty supply of available ash-constituents might be, on that account, incapable of assimilating air-food to the full extent of the atmospheric supply, and the amount of produce in such case would be small. By the death and decay of these plants, their ash-constituents would be restored to the land, so as to become capable of serving for a succeeding growth of plants, and the production of humus, at the same time, would provide in the soil itself a further source of air-food in addition to the atmospheric supply. Still the amount of produce from the succeeding growth would be small, if the available supply of ash-constituents remained as scanty as before. In this way vegetation might continue indefinitely without alteration, affording sustenance to numerous animals, as in the steppes of Central Asia, the prairies and pampas of America.

But if a larger amount of ash-constituents became available, in the interval between the successive growths, by the decomposition of minerals in the land, the conditions might become such as to ensure assimilation of air-food not only to the full extent of the atmospheric supply during the period of growth, but also from the further supply provided by the gradual decomposition of humus in the soil; and in such case the amount of produce would be proportionally increased.

The greater or less amount of available ash-constituents is, therefore, not the only condition upon which the amount of produce or the fertility of land depends, even in a strictly chemical sense; another essential condition is the amount of air-food capable of being supplied from within the soil, during the period of growth. Land, however rich in available ash-constituents—however well adapted in all other respects for prolific vegetation, would still afford but scanty produce without an ample supply of air-food during the period of growth. The increased supply of air-food provided by the decomposition of humus in the soil may be regarded, in this respect, as the accumulated atmospheric supply of several successive periods of growth; and the capability of land to furnish such a supply is, in a chemical sense, as much an element of its fertility as the available amount of ash-constituents it contains.

The requirements of different plants for such an augmented supply of air-food, in regard to the amount of produce, differ very widely, and the capability of different plants to assimilate the air-food thus stored up is also very different. The adaptation of the capability of one plant, in this respect, to provide for the requirements of another, and the development with that view of particular habits and conditions of growth in regard to certain crops, constitute the basis of the modern system of agriculture.

Having thus far described the general features of the chemistry of vegetation, in its simplest form, they must now be considered in their relation to agriculture; and it will be desirable first to examine the conditions affecting the supply of ash-constituents, as well as their influence under different circumstances.

In the cultivation of plants as a source of food for animals, and for other purposes, the ash-constituents requisite for vegetation are removed from the land in the produce; and since they are not replaced in the same manner as the atmospheric supply of air-food, the successive growth of a particular plant, year after year, would in process of time so far exhaust the land of available ash-constituents, as to render it incapable of supporting further growth, or of yielding such an amount of produce as would be worth the trouble and cost of cultivation. Hence arises the necessity of periodically returning to land under cultivation the ash-constituents thus withdrawn from it. Hence the practice, intuitively adopted in the rudest state of agriculture, of applying to land the excreta of animals fed upon its produce and the decaying refuse of the plants grown upon it. Such a system of cultivation would be sufficient to prevent any decrease in the annual produce of the land, inasmuch as the materials applied to it as manure, would restore whatever had been removed in the plants serving as food for animals, or for other purposes, and thus render the land capable of continuing—with the aid of the atmospheric sources of plant-food—to support vegetation. (See Kirwan, *Op. cit.* p. 160.)

If there were absolutely no export of produce, in such a case the restoration of the ash-constituents would be complete, and the capability of production would continue undiminished, so far as relates to the ash-constituents only. It would, in fact, increase year by year, so far as ash-constituents were concerned; for the available amount of them would be gradually increased by tillage, and by the consequent decomposition of minerals in the land. The improvement of the land by tillage is doubtless referable in some degree to such an unlocking of its natural resources, and the increase of what may be regarded as its floating capital in ash-constituents.

Where the population of a country is small and thinly distributed, and where land is of little value, as in many remote and uncivilised localities, all requirements may be fulfilled by such a system of relying upon the natural produce, without the need of any effort to increase it. But, even in such circumstances, it is seldom that the natural conditions of fertility are relied upon exclusively, or that the means adopted for maintaining the amount of produce are limited to the internal economy of the farm. Whatever fertilising materials can be obtained from external sources, at a cost commensurate with their capability of augmenting the produce, are generally employed as manure even in the rudest practice of agriculture. Guano has long been used for that purpose by the natives of South America (Humboldt, Fourcroy, and Vauquelin, 1803, *Ann. Chim.* lvi. 258–268). Fish, seaweed, &c., have been used from time immemorial as manure by the peasantry of seaboard districts; and wood-ashes, soot, &c., have been applied to the same purpose inland. Most of these materials would add to the amount of available ash-constituents in the land, and would in so far increase its capability of production.

Where, on the contrary, the population of a country was chiefly concentrated in centres, and a portion of the corn grown was annually removed from the land for the supply of food to towns at a distance, or under circumstances not admitting of the corresponding excreta being returned to the land as manure, the soil would be gradually deprived of ash-constituents, in a degree proportionate to the export of food. The internal economy of the farm would then no longer ensure the full restoration to the land of all the ash-constituents of its produce; it would no longer ensure the maintenance of the degree of fertility obtaining before the export of the produce commenced, or the capability of production corresponding to the amount of ash-constituents originally contained in the land. On the contrary, as the yearly export continued, and the abstraction of ash-constituents from the land progressed, the quantitative relation between them and the atmospheric conditions of vegetation at any place would be progressively changed; for while the atmospheric supply of air-food remained constant, the quantity of ash-constituents in the soil would diminish from year to year, until, eventually, vegetation might be no longer possible, in consequence of the deficiency of one of its essential conditions.

Even before that time, a point would be reached when the amount of produce would be no longer limited by the supply of air-food available from the atmosphere within the period of growth; when, on the contrary, the assimilation of air-food would be limited by the available amount of ash-constituents in the land, and when the amount of produce would be so small as not to be worth cultivation.

This exhaustion of land, or reduction of the degree of fertility, by the growth of successive corn-crops, and by the export of the produce, without any supply of manure from extraneous sources, would take place sooner or later, according to the nature of the land and the extent of its natural resources; sooner in the sandy or chalky soils, known as light land, than in the loamy or clay soils, known as heavy land. So far as the ash-constituents were concerned, the exhaustion of land might be retarded, under such circumstances, or the capability of production revived, by allowing it to remain at intervals without growing a crop on it for one or more years—a practice adopted under the name of bare-fallow. (See Kirwan, *Op. cit.* p. 160.)

During the interval of rest, a fresh supply of available ash-constituents would be provided for a future crop of corn by the decomposition of minerals in the land, thus compensating, either wholly or in part, for the abstraction resulting from export of produce. The amount of produce obtained, when a corn crop was grown, might in this way remain constant, or suffer but inappreciable diminution during long periods, especially in the case of rich soils. The rate at which the restoration of the ratio—previously existing between the supplies of available ash-constituents from the soil and of air-food from the atmosphere—took place, would depend upon the nature of the land and its tillage, and would determine the interval to elapse between the growth of two crops of corn.

The same result might be attained by a rotation of crops, or the alternate growth of different plants, occupying different ranges in the soil during their growth, or requiring different ash-constituents, such as corn and grass, or potatoes; so that, in either case, the ash-constituents contained in the land might be distributed among the different plants, and thus rendered available during a longer period. If the crops grown in the intervals between the corn-crops were consumed on the farm in feeding cattle, they would contribute to the production of manure; and, even if some of the cattle were exported, the greater part of the ash-constituents of the fallow-crops on which they had been fed, would remain upon the farm, and be returned to the land in the manure. However, the ultimate result of exhaustion would still be the same; and it has been long regarded as an established fact, that "the export of grain from a country, unless some articles capable of becoming manure are introduced in compensation, must ultimately tend to exhaust the soil. Some of the spots now desert sands in Northern Africa and Asia Minor were anciently fertile. Sicily was the granary of Italy; and the quantity of corn carried off from it by the Romans is probably the chief cause of its present sterility. In this island our commercial system at present has the effect of affording substances which in their use and decomposition must enrich the land." (Davy, *Op. cit.* viii. 78.—See Kirwan, *Op. cit.* p. 160.—Liebig, *Einleitung in die Naturgesetze des Feldbaues*, pp. 106–109.)

For the successful practice of agriculture, therefore, it is as necessary to maintain fertility, as it is to obtain a sufficient amount of produce. Land from which corn is exported requires, in most cases, a constant supply of manure from extraneous sources, capable of replacing the ash-constituents which may have been rendered deficient in amount.

An idea may be formed of the extent of the exhaustion of land from which corn is exported, by assuming that, in the countries which are the chief sources of corn, the amount of produce is at the rate of 15 bushels per acre, and that a corn-crop is grown every other year. The quantity of ash-constituents removed from the land per acre in the crop, would be about as shown the following table:—

Ash-constituents of Wheat, Barley, Oats.

		Total produce.	Corn.	Straw.
Amount of produce per acre		2260 lbs.	15 bushels	1333 lbs.
Total ash-constituents		92	15 lbs.	77
Comprising	Phosphoric acid	11	8	3
	Potash	14	4	10
	Lime and magnesia	8	2	6
	Silica	51	0	51

The greater part of these being contained in the straw, would be returned to the land in the farmyard manure; and if the whole of the corn were exported, without any supply of ash-constituents from without, there would be a permanent abstraction of them at the rate of 4 lbs. phosphoric acid and 2 lbs. of potash annually per acre. These being the substances which are least abundant in land, it is necessary that they should be restored again in some way.

But in order merely to maintain the degree of fertility, the supply from without does not require to be equal to the quantity removed in the exported produce; for land always possesses, in addition to its immediately available resources in ash-constituents, other resources which are latent—resources from which fresh supplies of them are only gradually developed, and rendered available by the operations of tillage in the manner already described. (See *ante*, p. 831, and Soils.)

Consequently, the exhaustion of soils, in regard to ash-constituents, though conceivable under such circumstances as those above referred to, is almost inconceivable, even in regard to ordinary land, under circumstances admitting of a proper supply of manure from extraneous sources, in addition to that produced upon the farm.

So far as the ash-constituents of land determine its share in the general conditions of fertility, it may be regarded as practically inexhaustible under any system of agricultural practice considered to be good merely from an empirical point of view, and having no higher recommendation than success.

The fertilising influence of manure is not, however, limited to the restoration of ash-constituents to land. It is also due to its capability of furnishing a larger supply of air-food to future crops, during their period of growth, than they could obtain directly from the atmosphere. This is one of the chief advantages resulting from rotation and the growth of fallow-crops for feeding cattle. The advantage of bare-fallow is also, to some extent, due to the accumulation of air-food in the soil, in virtue of its absorptive power. (See *ante*, p. 831, and SOILS.)

Since the available ash-constituents of land can be effective in determining an increased amount of produce, only in so far as they can co-operate with a proportionate supply of air-food during the period of growth, it is evident that the supply of this condition of fertility, by manure, must be of especial importance when it is necessary to obtain a large amount of produce.

The total resources of the generality of land in ash-constituents, preponderate so largely over the constant chemical conditions of fertility at any time available in the atmosphere, within the period of growth of ordinary crops—the latent resources of the land so easily admit of the liberation, from time to time, of fresh supplies of ash-constituents by the operations of tillage, that, under a good system of farming, the probability is rather in favour of the ash-constituents available at any particular time, being in excess of the supply of air-food directly available from atmospheric sources within the period of growth, and of that provided by manure resulting from the internal economy of the farm.

In some cases, the gradual unlocking of the latent resources of the soil by tillage, &c. may far exceed the yearly abstraction of ash-constituents. This chemical condition of fertility in land may increase from year to year, and, instead of retaining a constant proportion to the supplies of air-food from the atmosphere and from manure, it may preponderate over them; so that the amount of produce of the land in corn, might be increased, if the other chemical conditions of fertility were accessible in the same proportion within the period of growth. But though tillage, in such a case, would increase the fertility of the land, so far as the ash-constituents were concerned, it would not be attended with an increase in the amount of produce, unless it were accompanied by an increased supply of air-food during that period of the rotation when the crop, for which the liberated ash-constituents were most required, was growing.

The extent to which the accumulation of available ash-constituents in relative excess, may take place, is well illustrated by the experiments made at Rothamsted, on the growth of wheat, upon land which had been reduced to such a condition, in the ordinary routine, as to yield only half the average amount of produce in wheat. By the use of manure containing only the ash-constituents of wheat, on a plot of this land, the amount of produce obtained in 1844 was not greater than on the unmanured land. In the following year, the application of 336 lbs. per acre of mixed ammoniacal sulphate and chloride was attended with an increased amount of produce, amounting to double that obtained in the previous year from the unmanured land, or from that supplied with ash-constituents only. By continuing to grow wheat upon this plot of land for nineteen consecutive years with ammonia-salts only as manure meanwhile, the amount of produce obtained in each year continued to exceed that from the unmanured land; and the average amount of produce thus obtained, during the whole period, was only one-fourth less than it was in the first year, notwithstanding the very exceptional and continued drain on the ash-constituents of the land. (See Lawes and Gilbert—1847-64. *Op. cit.* viii. 226 xxv.)

Manure.		Amount of Produce per Acre.				Ash in Produce per Acre.		
		Dressed Corn.	Corn.	Straw.	Total.	Corn.	Straw.	Total.
		bushels.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
1844	Unmanured .	15	923	1,120	2,043	16	63	79
	Ash-constituents	15½	1,008	1,112	2,120	17	53	70
1845	Unmanured .	23¼	1,441	2,712	4,153	23	152	175
	Ammonia-salts .	32¾	1,980	4,266	6,216	30	202	232
Average of 19 years, 1845—1863	Unmanured .	16¼	1,031	1,723	2,754	18	96	114
	Ammonia-salts .	24½	1,575	2,737	4,312	25	128	153
Total in 19 years, 1845—1863	Unmanured .	310	19,597	32,740	52,337	338	1,824	2,162
	Ammonia-salts .	464½	29,932	52,008	81,940	465	2,440	2,905

In these results the influence of season in favouring or impeding the growth of wheat, was manifested by a certain variation in the amount and quality of produce under conditions otherwise similar; but this was not sufficient to obscure the differences referable to other causes.

The quantity of ash-constituents removed from the land during this period, without any such return as would have been made in ordinary practice, by the supply of farm-yard manure, affords still further evidence of the immense resources of the land in this particular, additional to that already referred to in the case of the unmanured land. (See *ante*, p. 831.)

Moreover, the absence of any increase in the amount of produce obtained in 1844 by applying to the exhausted land manure consisting only of ash-constituents of wheat, and the increase in the amount of produce obtained in the following year by using only ammonia, as compared with that on the unmanured land in 1845, are together most conclusive proof that, although in 1844 the chemical conditions of fertility were collectively insufficient for the growth of a full crop of wheat, still there was no deficiency in that element of those conditions which appertains exclusively to the soil—viz., the available amount of ash-constituents. Those results also prove, on the contrary, that in 1844 the available amount of ash-constituents in the unmanured land was far in excess of the other chemical conditions requisite for the growth of wheat—viz., the amount of air-food supplied, by the atmosphere and by the soil, during the period of growth. Consequently, the system of cultivation under which the land had become exhausted in regard to this crop, had admitted of a large accumulation of surplus ash-constituents, which would have remained useless in the land without a corresponding supply of air-food during the period of growth. The exhaustion consisted in the relative deficiency of air-food capable of being supplied from within the soil; and, therefore, increase in the amount of produce could only be effected by an artificial supply of air-food, additional to that furnished by the manure of the farm.

The practice of agriculture in many localities does not require that the amount of produce obtained should be very large: the only thing necessary, in many instances, is to maintain the degree of fertility, and the natural amount of produce is quite sufficient to be remunerative, as in those countries which are the chief sources of the supply of corn. In such cases, the manure produced by the internal economy of the farm may suffice to provide an adequate supply of air-food from within the soil.

In countries, however, where the population is dense, and land is of high value, agriculture assumes a very different character. Its object then is not merely to maintain a certain degree of fertility, but to produce, year by year, in the most profitable manner, and on a given area of land, the largest possible quantity of the materials of food for man and animals; to increase, by artificial means, the amount of produce upon an area incapable of yielding as much under natural conditions. (See Liebig—1843—*Chemistry in its Applications to Agriculture and Physiology*, 3rd edit. p. 112; Lawes and Gilbert—1847—*Journal of the Royal Agricultural Society of England*, viii. 227, xii., xvi. &c.)

Hence arose the idea of employing artificial manures—of augmenting artificially the chemical conditions of fertility. For the practice of agriculture under these circumstances, so utterly distinct from those of agriculture conducted only with a view to the produce of natural vegetation, the problem to be solved by the chemist for the guidance of the farmer is, what substances to supply as plant-food from extraneous sources, in order to obtain, year by year, a remunerative produce.

The question is mainly one as to manure: its solution, however, involves the consideration of conditions and reqirements other than those obtained in natural vegetation, not differing in kind, but quantitatively different. Still, the knowledge of the general phenomena of plant-nutrition must be the guide in the endeavour to solve this problem. Since it is established that the various materials of plant-food must bear a certain proportion to each other in order to be in the highest degree effective, and since the amount of produce is known to be limited by the quantity of that food-material which is present in least available amount, relatively to the requirements of any particular crop, the desideratum, in regard to the artificial means of increasing the amount of produce, is to ascertain what food-material becomes deficient, relatively to others, under the circumstances attending the growth of that crop. The deficiency may lie in the source of carbon or of nitrogen, in the supply of water or of available ash-constituents, or of some one of them; but whichever it be, the amount of produce will be limited by the deficiency.

The determination of that point will indicate, therefore, what food-material it is most necessary to supply artificially, in order to render effective in the highest degree those food-materials which are available in greatest abundance, relatively to the requirements of the crop in question. The food-materials least available abundantly in the same relation would be, in that particular case, the manure to be supplied artificially in order to obtain an increased produce. This is the fundamental principle of "high farming," which really consists in augmenting the acreage-produce—obtaining, year by year, crops larger than could be obtained under natural conditions—by rendering more effective the existing natural conditions of fertility.

This object may be attained in part by the right selection of artificial manure, so as to accumulate on the farm the materials of plant-food which are naturally most deficient, in regard to the whole of the crops grown in a series of years; and by adapting the method of cultivation so as to store up, during part of the rotation, the materials of plant-food which are relatively most deficient as regards a particular crop, grown at intervals, and to make that accumulation serviceable for increasing the amount of produce of that crop.

It is not by substituting for the manure produced by the internal economy of the farm, some one or other of its constituents, that this object is to be attained; but by supplementing it with what is most wanting, either naturally, or as the consequence of that branch of industry which is the business of the farmer—the manufacture of food.

Practically there is a limit to the increase of produce, besides that natural limitation which is due to climate and to season; it is the necessity that the degree of fertility produced and maintained should be remunerative. This purely commercial necessity introduces into the subject an important complication, involving the consideration of a number of circumstances which cannot be entered upon here, but which will readily suggest themselves to the reader.

In order to obtain such an amount of produce in corn as to be remunerative in this case, it is necessary to supply during the period of growth a larger quantity of nitrogenous air-food than would be furnished during that period by the atmosphere alone, or provided, in addition to that, by the internal economy of the farm, when no other crop but meadow-grass was grown besides corn.

This might be effected by the use of ammonia-salts as manure; but this source of ammonia is too limited to be alone sufficient in agriculture. Recourse is therefore had to the accumulation of ammonia from the atmosphere, by the growth of plants which possess the capability, under certain conditions, of appropriating nitrogen from that source, to a much larger extent than either wheat, barley, or oats, and which can be employed as food for cattle so as to produce meat—a marketable commodity equivalent to corn—and, at the same time, a larger supply of manure than could be obtained if the land remained in bare fallow, or were converted at intervals into meadow-land.

The manure so produced by the internal economy of the farm would contain the greater part of the nitrogen collected from the atmosphere by the crop intervening between the corn-crops, and used in feeding cattle, and would serve during the growth of corn to furnish the augmented supply of nitrogenous air-food necessary for obtaining a large crop of corn.

The plants which are cultivated mainly with this object may be represented by the turnip, since it presents a striking contrast to corn-crops, in regard to the conditions most favourable to increase in the amount of produce, as well as in regard to its capabilities and requirements, though it is inferior to leguminous plants in the power of assimilating nitrogen from the atmosphere.

The amount of produce obtained under the system of agriculture generally practised in this country is considerably higher with regard to all crops than it is in many other countries; and though there is a difference in this respect as to particular localities, the accompanying table may be taken to represent a fair average statement of the quantities of the several constituents of the different crops grown alternately in what is termed a "four-course rotation," when a crop of turnips, beans, or clover intervenes between two crops of corn.

The growth of the turnip as an agricultural crop, so as to obtain a large amount of produce, is far more liable to be influenced by differences of season than is the case with wheat. In the absence of rain, at a particular stage of growth, the greater number of the plants may die, and the acreage-produce become very small; but if the conditions of season be favourable, the amount of produce obtained may be as high as 20 or 30 tons per acre.

It has been supposed that the influence exercised by the cultivation of the turnip as a fallow-crop, in restoring and augmenting the fertility of land, and in conducing to the increase of the wheat-crop, was referable to its comparatively greater capability of appropriating, by means of its large leaf-surface, the atmospheric supply of air-food, during its period of growth, and to its requiring but a very small supply of food-materials from the soil. (See Davy, *Op. cit.* viii. 76, 77.)

That this is not the case, is evident from the amount of ash-constituents contained in the turnip, as shown in the table just referred to; and it is rendered still further apparent by the following results of experiments by Lawes and Gilbert (p. 840), showing the amount of produce obtained by growing turnips for three years consecutively on the same plot of land without manure.

Composition of the Acreage Produce of Different Crops.

		Corn Crops.			Root Crops.			Leguminous.	
Crop		Wheat.	Barley.	Oats.	Turnips.	Swedes.	Mangel.	Beans.	Clover-hay.
Amount of produce		30 bush.	40 bush.	44 bush.	10 tons.	13 tons.	16 tons.	34 bush.	5,000 lbs.
		lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Fresh crop	Grain or bulb	1,800	2,080	1,672	22,400	29,120	35,840	2,180	
	Straw or leaf	3,000	2,500	2,500	8,960	2,912	5,376	2,400	
	Total produce	4,800	4,580	4,172	31,360	32,032	41,216	4,580	5,000
Dry crop	Grain or bulb	1,530	1,716	1,438	1,792	3,203	4,301	1,809	
	Straw or leaf	2,520	2,175	2,075	1,165	379	537	1,968	
	Total produce	4,050	3,891	3,513	2,957	3,582	4,838	3,777	4,150
Ash-constituents	Grain or bulb	31	46	47	134	144	359	60	
	Straw or leaf	151	125	137	146	42	91	132	
	Total produce	182	171	184	289	186	450	192	373
Nitrogen	Grain or bulb	32	33	37	36	64	90	86	
	Straw or leaf	19	17	19	41	15	. .	27	
	Total produce	51	50	56	77	79	90	113	124
Phosphoric acid	Grain or bulb	15	15	10	13	14	18	20	
	Straw or leaf	8	5	6	7	3	5	9	
	Total produce	23	20	16	20	17	23	29	28
Potash	Grain or bulb	9	11	8	60	43	100	24	
	Straw or leaf	20	19	23	29	7	21	28	
	Total produce	29	30	31	89	50	121	52	75
Lime	Grain or bulb	1	1	2	16	16	13	4	
	Straw or leaf	8	11	10	44	12	8	28	
	Total produce	9	12	12	60	28	21	32	112
Magnesia	Grain or bulb	3	4	3	3	4	9	5	
	Straw or leaf	3	3	5	1	1	7	6	
	Total produce	6	7	8	4	5	16	11	32
Silica	Grain or bulb	1	13	22	1	2	9	1	
	Straw or leaf	101	75	68	2	1	2	5	
	Total produce	102	88	90	3	3	11	6	11

The immediate object of the cultivation of the turnip being the production of food for cattle, it is not required to reach maturity, as is the case with wheat; and it is desirable to obtain the utmost possible development of the fleshy root, so as to afford a food-material containing both nitrogenous and non-nitrogenous substances in fitting proportion for that purpose. During the early stage of growth, the young leaves of the turnip are liable to be attacked by insects, and it is therefore necessary to forward their development as rapidly as possible until the plants become sufficiently strong to resist this destructive influence. The number of plants per acre is therefore an important indication of the efficacy of the manures used.

The land selected for the experiments was a rather heavy loam, not of the best character for the growth of turnips; and three crops—wheat, clover, and wheat—had been grown upon it since it was manured. The variety of turnip grown was that known as Norfolk white. To ascertain the capability of appropriating the atmospheric food, and the relation which the turnip bore to the soil which was exhausted for wheat, a plot was left each year unmanured. On this plot the amount of produce was very small even in the first year, and in the third year the bulbs did not weigh more than two ounces each; so that in regard to the growth of the turnip, the resources of the soil are soon exhausted, and some supply of manure is evidently requisite for the growth of the turnip as a fallow-crop. (See Lawes and Gilbert—1847—*Op. cit.* viii. 38.)

Effect of various Manures on Growth of Turnips.

Plot.		Quantities of Manure per acre.	Number of plants per acre.	Average weight of bulb. lbs.	Amount of produce.		Dry substance.		
					Fresh bulb. lbs.	Fresh leaf. lbs.	Amount in bulb. per cent.	Nitrogen per cent.	Ash. per cent.
1843	2	Unmanured	17,940	0·52	9,382	Proportion of leaf to bulb greater in 1843 than in 1844.			
	1	12 tons farmyard manure	15,671	1·36	21,233				
	7	56 lbs. ammonia-sulphate	14,996	1·03	15,509				
	3	728 lbs. rape-cake	17,043	1·08	18,464				
	22	504 lbs. superphosphate	18,446	1·47	27,280				
	8	280 lbs. superphosphate, 420 lbs. rape-cake	16,096	1·69	27,158				
	18	Mixed phosphates, 551 lbs.	19,642	1·35	26,600				
1844	2	Unmanured	13,736	0·36	4,956				
	1	12 tons farmyard manure	20,096	1·19	24,108				
	22	Superphosphate, 560 lbs.	21,205	0·81	17,332				
	11	Superphosphate, 448lbs., rape-cake, 448 lbs., ammonia, 15 lbs.	10,320	1·29	13,328				
	18	Mixed phosphates, 448 lbs.	18,624	0·68	12,712				
1845	2	Unmanured	13,296	0·11	1,536	1,600	. .	3·31	4·22
		Top-dressing A. 1,120 lbs. rape-cake	24,944	0·67	16,816	10,832	8·68	2·17	
		B. 336 lbs. amm.-sulph.	15,456	0·07	1,082	744	8·71	2·98	
		A and B mixed	24,160	0·50	12,800	10,752	8·29	2·53	
		12 tons farmyard manure	23,731	1·61	38,170	16,560	7·83	1·56	8·24
		Top-dressing A. 1,120 lbs. rape-cake	. .	. .	. .	. .	7·92		
		B. 336 lbs. amm.-sulph.	23,104	1·45	33,472	22,392	7·30	2·54	
		A and B mixed	. .	. .	. .	. .	8·86		
	22	Superphosphate, 1,232 lbs.	24,352	1·17	28,432	9,856	8·24	1·58	6·99
		Top-dressing A. 1,120 lbs. rape-cake	23,544	1·33	31,416	13,440	7·83	1·89	7·21
		B. 336 lbs. amm.-sulph.	23,424	1·06	24,736	15,744	7·36	2·89	8·24
		A and B mixed	23,936	1·17	28,088	14,416	7·38	2·44	8·08
	18	Mixed phosphates	24,448	1·16	28,288	7,568	7·95	. .	6·99
		Top-dressing A. 1,120 lbs. rape-cake	23,404	1·33	31,216	12,576	8·36	. .	7·21
		B. 336 lbs. amm.-sulph.	24,448	1·18	28,778	13,600	7·42	. .	8·24
		A and B mixed	23,392	1·25	29,322	15,296	7·77	. .	8·08

With farmyard manure, which may be considered as supplying all the constituents of a large crop of turnips, the number of plants in each year represents the influence of season during the early stage of the growth; and the average weights of the bulbs represent the influence of season during the stage of bulb-formation.

Ammoniacal salts operated in most instances prejudicially during the earlier stage of growth, especially when placed near the seed; when used with farmyard or other carbonaceous manure, the development of bulb was in some instances considerable, and the development of leaf was much increased; but the amount of dry substance in these bulbs was generally less than in others, and the amount of nitrogen in the substance was greater—just the opposite of what happens in the growth of wheat.

With a considerable supply of ammonia, the vigorous growth of the plants was accompanied by a less rapid advance towards maturity in the bulb, and a condition less favourable for providing a supply of root-food than for the production of seed by further growth. In this respect the influence of artificial supply of ammonia upon the amount of produce of the turnip-root and of wheat, presents a striking contrast; and it is evident that in the cultivation of the turnip for feeding purposes, and as a fallow-crop for obtaining a supply of manure, it is capable of appropriating nitrogen from the atmospheric supply during its period of growth, or from within the soil, to such an extent as not to require any considerable supply artificially by means of manure.

The influence of soluble phosphates in promoting the early growth of the plants is well indicated in each year by the number of plants, both when used alone and with other manures; but it is only during that stage of the growth that they contribute to increase the amount of produce in bulbs, as will be seen by the small average weight of the bulbs grown with phosphates only supplied as manure.

In the plots supplied with manure capable of furnishing a considerable amount of carbonaceous air-food, the development of the bulbs, indicated by their average weight, was much more considerable than in any other case, except where soluble phosphate was used in the first year, and where the exceptional result was probably referable to carbonaceous substances in the soil. The influence of a supply of air-food from within the soil, upon the development of bulb, is still more strikingly illustrated by the contrast between the second and third year's results. Though with soluble phosphates alone or with other manure, the number of plants was always considerably greater than in their absence, the average weight of bulbs was very small; while on the plots where phosphates were used together with a carbonaceous manure, the average weight of the bulbs indicates a much larger bulb-development. That, together with a greater number of plants, gave consequently the largest amount of produce.

The necessity for the presence of carbonaceous substances capable of supplying food-material from within the soil, is rendered more strikingly evident by the results of the second year; for although the season was, on the whole, more favourable than that of the preceding year, and though the number of plants was greater, the amount of produce was generally less, in consequence of the slower rate of growth and bulb-formation. In the third year, also, the deficient bulb-development within the period of growth, on those plots where phosphates alone were used, as compared with the results obtained where carbonaceous manures were also supplied, shows the importance of providing that source of plant-food in order to insure rapid growth, and to obtain a large amount of produce.

The influence exercised upon the composition of the bulb by the ratio existing between the supply of carbonaceous and nitrogenous air-food from within the soil, is well indicated by the differences in the amount of nitrogen in the dry substance of the turnips grown with farmyard manure and rape-cake alone, and with addition of ammonia, and in those grown without manure and with top-dressings containing different proportions of carbon- and nitrogen-yielding materials.

Carbonaceous manures, however, are serviceable only in the later stage of growth by affording a supply of food-material for the development of bulk; and in the earlier stage of growth they may even be prejudicial if placed near the seed, as indicated by the smaller number of plants in the first two years when these manures were drilled with the seed. They should, therefore, be placed so as to be only within reach of the young plant when it has developed its accumulative organs under the influence of the phosphate, which should be placed as near as possible to the seed. The advantage of doing so is illustrated by the greater number of plants in the third year, when these manures were applied as a top-dressing to the land.

Comparing these results with the quantity of phosphoric acid contained in the turnip, it will be seen that the influence of phosphates on the growth of this plant cannot altogether be referred to the mere supply of material serving for the production of plant-substance by becoming a constituent of it. Though the amount of phosphoric acid in the turnip-crop is not larger than that in the wheat-crop, a direct supply of soluble phosphate appears, from very general experience, to be much more influential in regard to the development of the turnip than in the growth of wheat. Hence it is scarcely possible to avoid the conclusion that it exercises some important and essential function in that particular mode of development requisite in the cultivation of the turnip as a fallow- and feeding-crop, other than that which is represented by the amount of phosphoric acid contained in the plants.

In these experiments the supply of potash as a constituent of manure was not found to exercise any favourable influence, either upon the mode of development of the turnip-plant, or upon the amount of produce; nor was it to be expected that this land, which was capable of growing wheat without manure for several consecutive years, should be at all deficient in supply of potash for the growth of a turnip-crop, although the quantity of potash required by it is so much larger than that needed for wheat.

The quantity of potash removed from the land in the turnip-crop does not cause exhaustion of the ash-constituents to any sensible extent; for, excepting a small portion exported in the meat produced by the use of the turnip in feeding live-stock, they are again returned to the land in the manure; and if artificial phosphate-manures be employed in the cultivation of turnips, the abstraction of this constituent from the land by the export of corn will be to a great extent compensated, if not covered.

The facts already described will serve to show that the cultivation of the turnip is a part of the economy of the farm, by means of which nitrogen is stored up as part of the floating capital of the land, and, after having served intermediate purposes, is made to contribute to the important result of increasing the amount of produce in corn. It is by this means that concentration of the atmospheric supply of nitrogenous plant-food is effected, so as to furnish the corn-crops, during their period of growth, with twice as much as they could otherwise obtain directly from that source by their own unaided capability of appropriation.

Though the turnip has here been referred to as a plant presenting, in the circumstances of its cultivation, a strong contrast to corn-crops, it is chiefly by the growth of leguminous crops—such as clover, beans, and tares—that nitrogen is directly appropriated from the atmosphere. In the cultivation of the turnip as a fallow-crop an artificial supply of nitrogen over and above that provided by the farm manure is not generally requisite; but it draws largely upon the supplies of nitrogen from within the soil; and in this respect it tends to render an artificial supply of nitrogenous manure more necessary for the succeeding corn-crop (Lawes and Gilbert, *Op. cit.* xviii. 454; *Journ. Chem. Soc.* [2] i. 100). Leguminous crops, on the contrary, appear to render land richer in nitrogenous supply, and thus to augment its capability of yielding large crops of corn. The influence of clover in this respect has long been known. (See Kirwan, *Op. cit.*, p. 166.)

In the cultivation of land under such circumstances, supposing the amount of produce sold during 4 years to be 30 bushels wheat, 35 bushels barley, and the live-weight produced from 10 tons turnips and 5,000 lbs. clover-hay, or 1,500 lbs. beans, without imported food, the quantity of ash-constituents removed from the land would be, at the utmost, as shown in the following table:—

Quantities of Ash-constituents per Acre abstracted from Land, in Produce sold off the Farm during Four Years.

	1st Year.	2nd Year.	3rd Year.		4th Year.	Average Quantity per Acre,	
	Live-Weight from Turnips.	Barley.	Live-weight from Clover-hay	or Beans.	Wheat.	in Four Years.	per Annum.
Amount of produce.	10 tons.	35 bushels.	5,000 lbs.	1,500 lbs.	30 bushels.		
Fresh produce .	22,400	1,820	5,000	1,500	1,800		
Dry produce .	2,464	1,529	4,200	1,260	1,530		
Nitrogen . .	. .	30	. .	. .	32		
Total ash .	2.46	40·5	3·13	1·58	31	76	19
Phosphoric acid	0·98	13·4	1·05	0·63	15	30	7·5
Potash . .	. .	9·75	0·16	0·09	9	19	4·8
Silica . .	. .	11·4	. .	. .	0·6	12	3

It now only remains to consider the means of maintaining the supply of carbonaceous material requisite as one of the conditions of the production of the full amount of produce in turnips. In the feeding of animals there is a loss of carbon, due to respiration, amounting to nearly one-half of that contained in the food. It is therefore necessary to increase as far as possible the quantity of manure produced by the internal economy of the farm, by the use of imported food-materials in feeding cattle. This is at once a profitable mode of converting those materials into a more valuable commodity, and of obtaining a larger quantity of manure for the cultivation of crops; thus maintaining, or even increasing, the fertility of the land, by bringing upon the farm ash-constituents—which compensate for the export of corn—and materials containing nitrogen and carbon in a form capable of becoming available in the cultivation of crops as supplies of air-food, auxiliary to those furnished by the atmosphere and by the farm-yard manure resulting from the crops grown.

On a farm cultivated under such a system, the exhaustion of the land is altogether precluded; and although the existing system of disposing of town-refuse involves a total loss of the phosphates and potash contained in the exported produce, it is probable that, as regards the extent of land at present under cultivation, there may be sufficient available sources of those substances in the mineral kingdom, to counterbalance such a loss for a long time to come. Still, the disposition of town-refuse in such a manner as to be available in fertilising land, and to be useful rather than a source of injury and annoyance, is a requirement which is every day more urgently demanding attention.

Having thus considered the nature of the differences obtaining, on the one hand, between spontaneous vegetation altogether unaided by art, and natural vegetation assisted by tillage—on the other, between agriculture conducted only with a view to obtaining the natural amount of produce, and agriculture involving an increased produce by artificial means, it is now necessary to consider what applications have been made of the general knowledge of the chemistry of vegetation, or of the views which have been entertained with regard to it.

Liebig, in applying to agriculture the theory of plant-nutrition which he constructed from the materials furnished by **Saussure**, **Davy**, **Sprengel**, and **Boussingault**, adopted the fundamental proposition, that plant-food consists solely of carbonic acid, water, ammonia, and the ash-constituents. In endeavouring to ascertain the causes of the efficacy of manure; the mode in which it acts; the circumstances upon which different methods of culture depend; and to establish rules for a rational system of agriculture,—he addressed himself first to the questions, "What does the soil contain? What do the materials called manure contain?" as questions whose determination constituted the starting-point of rational agriculture (*Chemistry*, &c., 1st edit. p. 139). In this enquiry his attention was mainly directed to the ash-constituents of plants, and to the comparison of these with the constituents of soils and of manure. Observing that all cultivated plants contained potash, phosphoric acid, and other ash-constituents; that the presence of these substances was constant in particular plants, and parts of plants; that every productive soil contained the same substances; that the repeated successive growth of a particular crop on the same land rendered it less capable of producing that crop until an interval of some years had been allowed to elapse without growing it,—he came to the conclusion, that the capability of land to produce crops, was due to the presence in it of the ash-constituents of plants; that the assimilation of carbon and nitrogen was dependent upon the presence of the ash-constituents in the soil, and limited by the available amount of them: consequently, that the amount of produce was proportionate to the available amount of ash-constituents in the soil (*Op. cit.* 3rd edit. pp. 113–123). From the same data he concluded that the decrease of produce observed when a particular crop is raised year after year on the same land, was due to the abstraction of ash-constituents from the soil. (*Op. cit.* pp. 118, 164.)

Observing, further, that animal excreta and the plant-remains in farmyard manure contained the same ash-constituents as the plants which had been consumed as food; that this manure exercised a fertilising influence upon land naturally unproductive, or exhausted by the cultivation of crops,—he concluded that the efficacy of this manure, which might be regarded as the ashes of the food burnt in the bodies of animals, was due to the ash-constituents it contained; that its peculiar action consisted in and was limited to the supply or restoration of the ash-constituents, which the land was either destitute of or had been deprived of by previous crops. (*Op. cit.* pp. 176–187; *Address to the Agriculturists of Great Britain*, pp. 7–12.)

From the well-known facts that the produce of land could be increased by manure, and that in many cases the crop is directly proportionate to the quantity of manure used, he concluded that this effect was referable to the amount of ash-constituents supplied to the land; that if the supply of those constituents were greater than the quantity taken away in the previous crop, the amount of produce would be increased; that if the supply of them were less than that, the produce would be reduced; and that if it were just equal to the quantity removed, the produce would remain constant. (*Address*, pp. 7–12.)

Adopting these conclusions as axioms to be observed in practical agriculture, **Liebig** also taught that the production of the organic constituents of plants from carbonic acid, water, and ammonia was determined by the presence of the ash-constituents proper to the plants cultivated (*Chemistry*, &c., pp. 196, 204); that its extent was limited by the available amount of them in the soil (*Op. cit.* p. 203); that the efficacy of humus in augmenting the amount of produce, by furnishing a supply of carbonic acid additional to that afforded by the atmosphere, was subject to the same limitation (*Op. cit.* p. 197); that the amount of produce was so entirely independent of the artificial supply of ammonia, that if only the ashes of solid and liquid excreta were supplied as manure, the crops cultivated would derive their carbon and nitrogen from the atmosphere (*Op. cit.* pp. 181, 203–204); that the ammonia of the atmosphere, exceeding the requirements of wild plants, was fully sufficient for all the objects of agriculture, even for that most important one, the production of nitrogenous constituents of plants to serve as food for man and animals. (*Op. cit.* pp. 54, 211.)

The production of these substances was represented by **Liebig** as depending upon the presence, in the soil, of phosphates, which enabled plants to derive the requisite nitrogen from the atmosphere—a source where the abstraction of that element was spontaneously compensated by the ammonia resulting from the decay of animals and plants, and perhaps from other sources (*Op. cit.* pp. 147, 212). He also insisted that it was of the greatest importance for agriculture, to know with certainty that the artificial supply of ammonia was unnecessary and superfluous for the growth of most cultivated plants, and that the value of manure could not be estimated, according to the rule recognised in France and Germany, by the amount of nitrogenous substances it contained. (*Op. cit.* p. 213.)

To give still greater prominence to his opinion as to the superfluity of nitrogenous manure, **Liebig** instanced the large quantity of nitrogenous substances produced—as hay, milk, and flesh—on grass-land without any supply of nitrogenous manure, and contrasted that fact with the smaller produce of nitrogenous constituents produced, within the same period—as corn and roots—on land to which nitrogen had been supplied as manure in greater quantity than was contained in the produce. He also referred to the export from Egypt of ammonia, obtained by burning animal excreta; to the proverbial fertility of that country, where only the ashes of excreta, and the Nile mud, containing little nitrogen, had been used as manure for ages; to the export of cheese from Holland and Switzerland,—as rendering it perfectly certain that the prodution of nitrogenous constituents of plants was not proportionate to the quantity of nitrogen supplied to the land in the manure: that the export of nitrogenous produce was not exhaustive; because it was not the soil, but the atmosphere, which yielded nitrogen to plants: that it was impossible to augment the produce of land by the supply of highly nitrogenous manure, or of ammonia-salts alone; but that, on the contrary, the capability of land to produce crops increased or diminished in direct proportion to the ash-constituents supplied to it in the manure. (*Op. cit.* pp. 210, 211.)

The logical consequence of the opinions thus formed, was to regard the ash-constituents as the essentially, if not the only, effective portion of manure (*op. cit.* p. 202). It was insisted upon as a point of especial importance for the practical farmer not to deceive himself concerning the cause of the efficacy of manures (*Op. cit.* p. 187). In this respect the ash-constituents were compared by **Liebig** to the quinine of cinchona-bark, the iodine of burnt sponge, or the active principles of opium (*Op. cit.* p. 187). Consequently, the ash-constituents of manure were the materials which, according to his view, it was essential for the farmer to supply to land artificially, in order to increase the amount of produce. (*Op. cit.* p. 203, 211.)

The fundamental principle of rational culture, according to that view, was the perfect restoration of the ash-constituents removed from the land; and whether that restitution were made by applying excreta, or ashes, or bones, was regarded as a matter of indifference (*Op. cit.* p. 187). The particular kind of ash-constituents to be used as manure, was to depend upon the kind of produce required; alkalis for the production of substances analagous to starch; phosphates for the production of nitrogenous substances (*Op. cit.* pp. 193, 142, 144, 148). By the exact determination of the amount of ash in cultivated plants, and by the analysis of the ashes, the quantities of these substances removed from land by crops was to be ascertained. Thus the farmer was to be enabled to keep a debtor and creditor account, for each of his fields, of the several ash-constituents removed from the land, year by year; and to determine, according to the kind and quantity of the crops raised upon it, what substances and what quantities of them were to be returned to the land, in order to restore its original condition of fertility, or to be able to express exactly how many pounds of one or other constituent was to be supplied to the land in order to augment the amount of produce. (*Op. cit.* pp. 213, 214.)

Extending this view of the chemistry of plant-nutrition to the explanation of the various operations of the farm, the practices of rotation, fallow, &c., **Liebig**, still concentrating his attention upon that particular aspect of the chemistry of agriculture in which the ash-constituents of plants, soils, and manure are concerned, ascribed the influence of fallow in rendering land again capable of supporting the growth of corn, solely to the liberation of the ash-constituents requisite for that crop, by the decomposition of alkaline silicates in the land during the interval of fallow (*Op. cit.* pp. 118, 130–133). The similar influence of burnt lime and burnt clay on some soils, was ascribed to the same cause (p. 136). He represented the advantages of rotation of crops as being, to some extent, due to the production of humus in the soil, but chiefly to the unequal requirements of the different alternating crops for particular ash-constituents, and to the consequent accumulation, during the greater part of the period of rotation, of those ash-constituents present in least available amount in the soil, and requisite for the growth of one crop in larger amount than for the growth of the intervening crops. (*Op. cit.* pp. 150–161, 169, 172; **Berzelius**—1844—*Jahresbericht*, xxiv. 333.)

This theory of the chemistry of agriculture was applied by **Liebig** in the production of artificial manure; and a patent was obtained by **Muspratt** for the method of manufacture, as a communication from **Liebig** (*Improvements in the Manufacture of Manure*, 1845, Specification No. 10,616). These artificial manures were intended to supply to the land exactly what was wanting for the growth of any particular crop, and thus to effect an economy which would be impossible while manure was applied indiscriminately—the useful and the unnecessary constituents together. But the chief advantages which these artificial manures were to secure, were to render the rotation of crops and fallowing unnecessary and superfluous, and to admit of one and the same kind of crop being grown, year after year, upon the same field—of a perennial wheat-crop without the necessity either of fallow or of a rotation of crops, which was regarded by

Liebig as a restriction excluding all that science might be able to teach (*Principles*, p. 47). These manures, which were intended to effect such an entire revolution in agricultural practice, consisted chiefly of compounds of potassium-carbonate, with calcium-carbonate or phosphate, potassium-silicate, gypsum, bone-earth, and salt, and about 4 per cent. ammonio-magnesian phosphate, equivalent to rather less than 0·25 per cent. ammonia in the manures. The following table contains analyses of these manures, as manufactured by Messrs. Pfeiffer, Schwarzenberg, & Co. in Cassel (Pabst —1849—*Landwirthschaftliche Erfahrungen von Hohenheim*, p. 13). For the sake of comparison, the calculated composition of the manures, according to the directions of the specification, is added:—

Composition of Liebig's Artificial Manures.

		For Cereals.		For Leguminous Crops.		For Root-Crops.		For Tuber-Crops.
			Calculated		Calculated.		Calculated.	
Soluble in hydrochloric acid.	Ammonia .	. .	0·28	. .	0·24	. .	0·40	
	Potash . .	9·30	40·32	11·38	26·28	14·60	19·10	15·31
	Soda . .	10·00	4·72	13·70	13·20	4·02	15·73	3·33
	Lime . .	21·20	9·16	25·23	16·20	32·20	20·05	26.15
	Magnesia .	3·75	0·64	1·67	0·64	1·55	1·06	2·92
	Ferric oxide .	5·05	. .	1·48	. .	1·36	. .	6·35
	Phosphoric acid	5·50	6·00	1·50	9·76	2·37	14·20	0·22
	Sulphuric acid.	10·08	3·72	9·17	3·72	6·70	3·06	9·67
	Chlorine . .	1·04	. .	1·16	2·40	1·68	. .	1·14
	Carbonic acid .	9 82	7·56	14·33	16·48	25·20	21·60	19·47
	Insoluble in HCl	24·30	. .	18·39	. .	9·08	. .	18·40
	Silica . .	. .	26·00	. .	8·32			
	Water . .	. .	3·00	. .	2·96	. .	4·50	
		100·04	100·00	98·01	100·00	98·76	100·00	99·12

The proper composition of manures for other plants, was to be ascertained by burning the plants, and analysing the ashes, and then combining the manure according to the analysis ("*Specif.*" p. 4, line 27). In the *Address to Agriculturists*, explaining the principles of artificial manuring, Liebig stated his view that "the exhaustion of the soil by subsequent crops—its decrease in fertility—is produced by the gradual removal of the mineral elements, in a soluble state, which are necessary for the development of our cultivated plants. By a supply of manure they are again restored to the state suited to serve as nourishment to a new vegetation. If the supply of the removed elements of the soil, by means of manure, be sufficient, if the quantity taken away be restored, the original fertility reappears; if the supply be greater, the produce increases; a defective supply gives a smaller produce" (p. 12); or, in other words, the amount of produce was directly proportionate to the available quantity of ash-constituents, or mineral substances which, "as such, are indestructible by fire, and consequently remain as ashes after the incineration of the plants, or of their parts." (p. 8.)

Consequently, the agriculturist was to confine himself to supplying these substances to his land, and giving it the proper physical condition, so as to render possible, and to increase, the assimilation of carbonic acid and ammonia from the atmosphere.

This theory of agriculture, or of manures—known as the mineral theory—was received with enthusiasm in England and America, and the estimation in which it was held is well represented by the following comments, published shortly after the introduction of the new manures:—"Since the organic food-materials are universally supplied to plants in constant amount, the great difference of vegetation cannot be sought in them, and, consequently, must be due to the inorganic constituents; so that, in putting farm-manure upon land, it would be essentially quite the same if it were first burnt, and only the ashes strewed upon the land, since its efficacy can only be due to its ash-constituents. It is easy to perceive that this principle, applied to agriculture, suddenly sheds a new light upon all phenomena whose explanation has hitherto been sought for in vain. Now, it is easy to conceive why irrigated meadow-land can yield annually great quantities of hay without manure when the necessary quantities of salts are conveyed to it in the water. It becomes clear how the Peruvian is able to obtain luxuriant crops of maize upon the most arid sand-drifts, if only a tiny rill from the snow-peaks of the Andes conveys to them the requisite soluble earths. Hundreds of similar phenomena are elucidated by this ingenious idea of Liebig's; but hundreds of new ideas are also suggested fruitful in development and improvement for that simplification and security of agriculture which will be the inheritance of posterity; and we begin to find it natural that in England—where, according to the standard hitherto known, agriculture stands so high—Liebig should be celebrated as the founder of a rational system, in opposition to the previous purely empirical one; and that he should be overwhelmed with laudatory demonstrations and marks of honour, in such a way as scarcely any one, and certainly no foreigner, has ever experienced there."—Schleiden, *The Plant*, pp. 173-174.

Under the auspices of the Royal Agricultural Society of England, an elaborate investigation of plant-ashes was undertaken by Way and Ogston, with the view of obtaining data for the preparation of artificial manures according to Liebig's mineral theory of agriculture (*Journ. Roy. Agric. Soc.*).

But experience did not realise the expectations which had been entertained as to the results to be obtained by the use of manure prepared according to the principles of the "mineral theory." Among other places, the wheat-manure was tried at Rothamsted, and the following results were obtained. (See Lawes and Gilbert, *op. cit.* viii. xxv.)

Plot.		Dressed corn per acre.	Weight per bushel.	Total corn.	Straw.	Total produce.
	1843–44	bushels.		lbs.	lbs.	lbs.
3	Unmanured	15	58·5	923	1,120	2,043
2	Farmyard manure, 14 tons	20⅓	59·3	1,276	1,476	2,752
4	Ashes of ditto "	14½	58·0	888	1,104	1,992
10	Superphosphate, 560 lbs.; potash-silicate, 220 lbs.	15½	62·0	1,008	1,112	2,120
17	Mixed phosphates, amm.-sulph., 65 lbs. .	19	62·3	1,240	1,422	2,662
19	" " " " 81 lbs. .	24⅛	61·8	1,580	1,772	3,352
	1844–45					
3	Unmanured	23	56·5	1,441	2,712	4,153
2	Farm-yard manure, 14 tons . . .	32	56·8	1,967	3,915	5,882
6	Superphosphate, 112 lbs.; ammonia-sulph., 112 lbs.; rape-cake, 560 lbs. . . .	28¾	57·8	1,871	3,644	5,515
10	Amm.-sulph. and chloride, 336 lbs. . .	32	56·3	1,980	4,266	6,246
	1845–46					
3	Unmanured	18	63·8	1,207	1,513	2,720
2	Farmyard manure, 14 tons . . .	27	63·0	1,826	2,454	4,280
6	Liebig's manure, 448 lbs.	20⅛	63·7	1,400	1,676	3,076
	" " " amm.-salts, 224 lbs.	29¼	63·5	1,967	2,571	4,538
7	" " " rape-cake, 448 "	22¾	63·0	1,534	1,968	3,502
	" " " amm.-salts, 224 " & rape-cake, 448 "	31¾	63·4	2,163	3,007	5,170
10	Ammonia-sulphate, 224 lbs.	27⅛	63·6	1,850	2,244	4,094
	Unmanured	17⅜	63·8	1,216	1,455	2,671

Comparing the amount of produce obtained by the use of farmyard manure, with that obtained where only the ash of an equal quantity of the same manure was used, it is evident that the use of this manure effects something more than the mere restoration of ash-constituents to the land: and this result alone is sufficient to show the error of the "mineral theory of agriculture."

It has already been shown that the land, though exhausted in regard to the growth of wheat under the ordinary system of cultivation, was still rich in available ash-constituents (see *ante*, p. 837): consequently, the application of these only as manure, was not attended with any increase of produce over that obtained without any manure, which may be regarded as the measure of the extent to which the natural supply of air-food by the atmosphere and soil was available for the growth of wheat. But, wherever ammonia was supplied as manure, the produce was always much increased, even in those exceptional instances where it was used alone. These results, then, are in direct opposition to Liebig's mineral theory of agriculture.

In the case of wheat, the capability of production does not increase or diminish in exact proportion to the ash-constituents supplied to land in manure, but the amount of produce is proportionate to the supply of nitrogen in the manure; the capability of production may be increased by manure rich in nitrogen, and even by ammonia-salts alone. (See Chatterley—1843—*Phil. Mag.* xxii. 470: Report of some experiments with saline manures, containing nitrogen.)

It is, therefore, the relative deficiency of the supply of nitrogenous food which must be regarded as constituting the principal feature of that exhaustion of land, in regard to the growth of wheat, which takes place in the ordinary routine of agricultural practice.

Similar experiments to those above described have been made on the light land of Norfolk and in Kent, and the same general results have been arrived at. (See Lawes and Gilbert, *Op. cit.* xvi. 207. xxiii. 31.)

These facts at once furnish a clue to the function of farmyard manure in the growth of wheat, over and above the mere restitution of ash-constituents, and they illustrate the importance of the accumulation of available nitrogen upon the farm by the cultivation of fallow-crops. Moreover, they are conclusive proof that, so far as relates to increase of produce in wheat, the value of this manure is more essentially dependent upon the supply of nitrogenous material which it provides, than upon the restoration of ash-constituents removed by former crops; though this latter is a necessary condition of the maintenance of fertility in regard to long periods of time, and one which always obtains under a good system of farming.

The striking contrast presented by wheat and turnips in regard to amount of produce, when grown year after year on the same land without manure, clearly indicates that, in the cultivation of the turnip, by which the exhaustion of land, by previous crops, is compensated for in ordinary practice, a supply of air-food from within the soil requires to be provided by manure. Though the produce of wheat—allowing for the influence of season—was tolerably constant during twenty consecutive years, the produce of turnips was reduced in three years to almost nothing. Consequently, the capability of this plant to appropriate the food-materials furnished by the atmosphere during its period of growth, is not so great as has been supposed, and is, indeed, inferior to that of wheat.

The different value of manure in regard to these crops respectively, is also shown by the results obtained with phosphates, with ammonia-salts, and with farmyard manure. Superphosphates applied to wheat afforded no increase in the amount of produce over that obtained without manure; but with turnips it always increased the amount of produce, especially when there was an abundant supply of carbonaceous air-food provided, in addition to that furnished by the atmosphere within the period of growth. Ammonia-salts applied to turnips, either with or without other ingredients of manure, and with abundant supplies of ash-constituents in the land, did not increase the produce, or promote a favourable mode of growth; but with wheat, under the same conditions, they often doubled the amount of produce. Farmyard manure—containing both phosphates and ammonia, or its equivalent, together with a large amount of carbonaceous material—applied to wheat did not increase the amount of produce more than 50 per cent. over that obtained without manure; but with turnips its use was attended with large increase in the average weight of the bulbs; and when soluble phosphates were also used, there was a very considerable increase in the amount of produce per acre. The difference in these cases is chiefly referable to difference in the requirements of these plants as they are cultivated; a comparatively more abundant supply of carbonaceous food and of phosphates being necessary for the turnip, while wheat requires a comparatively more abundant supply of nitrogenous food.

The amount of produce obtained with Liebig's wheat-manure, in the third year, was little above that obtained without any manure, and much less than that obtained with farm-yard manure; but when ammonia-salts were used with Liebig's manure, the amount of produce was increased nearly in proportion to the amount of nitrogenous material supplied either as ammonia-salts or rape-cake.

Experiments made before 1845 by Liebig himself, with these manures consisting only of ash-constituents, did not furnish any indications of their efficacy; and in subsequent trials upon poor uncultivated land at Giessen, the effect produced where they were used alone was very slight, compared with that where forest-earth or stable-manure were used (Liebig, *Principles*, pp. 40–45). By cultivation, the fertility of the land gradually increased; but as no data have been given as to the composition of the soil, the amount of produce, &c., by which an opinion could be formed as to what were the latent resources of the land—how much of the result may be due to the influence of tillage, or to the manure produced as the result of cultivation only, and how little of that result may be due to the supply of ash-constituents to the land in the first year—it is impossible to regard the results of these experiments as constituting any exception to the observations made elsewhere as to the effect of manure consisting wholly of ash-constituents of plants.

The failure of Liebig's wheat-manure, and the inefficacy of the ash of farm-yard manure have been ascribed to their deficient solubility. (See Liebig, *Einleitung in die Naturgesetze des Feldbaues*, pp. 70 *et seq.*; International Exhibition, 1862, *Reports by the Juries*, p. 161.) This opinion may be urged as an excuse in those instances, but it has no applicability to the other instances in which the constituents of the wheat-manure and of the ashes were used in a very soluble condition, and were nevertheless equally inefficient in augmenting the produce beyond that obtained without manure. The state of exhaustion could not, therefore, consist in deficiency of ash-constituents; and the results obtained by the use of ammonia, even alone, or with those manures, clearly prove that the relative deficiency of nitrogenous supply within the period of growth, was the main feature of the exhaustion, the determining cause of the small amount of produce on the unmanured land, and of the inefficacy of the soluble ash-constituents, if not also of the farmyard manure ash and of **Liebig's** manure.

These results, therefore, show that all hope of obtaining annual crops of corn, or of increasing the amount of produce of crops generally, by means of manures consisting only of the ash-constituents of the plants grown, must be entirely abandoned; and that, as regards agricultural practice, precisely the opposite course must be adopted, of supplying air-food by artificial means, in order to render the available resources of the land fully effective. The artificial supply of nitrogenous air-food is the only means by which a full agricultural crop of corn can be obtained year after year from ordinary land. But since the sources of ammonia-salts at present available are inadequate for that purpose, it is evident that a rotation of crops is an indispensable feature of a system of agriculture where the production of corn is the chief object, and where it is necessary to obtain a large amount of produce. The increased supply of nitrogen stored up from atmospheric sources by the cultivation of fallow-crops, and made available by cattle-feeding for the production of corn, must at the same time be supplemented by the purchase, from extraneous sources, of nitrogenous manures, and cattle-food, as far as may be practicable and profitable in particular instances. In the case of land rich in ash-constituents, the artificial supply of nitrogenous manure may be, to some extent, substituted for rotation, and cattle-feeding, so as to obtain larger and more frequent corn-crops.

It appears, therefore, that instead of reforming agriculture by his manures, **Liebig** caused them to demonstrate the incorrectness of his mineral theory of agriculture; and the failure of those manures, from the application of which farmers had been induced to anticipate such wonderful results, naturally produced a revulsion of opinion which was sometimes expressed in a manner not altogether free from exaggerated opposition to the views put forward by **Liebig**. Thus the President of the Royal Agricultural Society of England, after remarking, in his annual address, that "the mineral theory, hastily adopted by **Liebig**, had broken down; and that the doctrine of the increase or diminution of crops being exactly proportionate to the increase or diminution in the quantity of ash-constituents supplied to them in manure, had received its death-blow from the experiments at Rothamsted," went on to state, that of the active principles of manure, ammonia was specially suited for corn, phosphates for turnips. (**Pusey**—1850—*Jour. Roy. Agric. Soc.* xxii. 383–392.)

This expression of opinion by a practical farmer must be regarded as applying chiefly to the artificial supplies of manure required for different cultivated plants, and not by any means indicative of the idea that, in regard to the nutrition of plants considered apart from agriculture, any one or other constituent of plant-food possessed a special value independent of others. The erroneous estimate **Liebig** has formed of the opinions held in this country respecting manure, has no other basis than the supposition that such an idea has been entertained, or else the want of a due comprehension of the farmer's strictly technical view of this subject being limited to the consideration of materials to be provided over and above those supplies which are furnished by ordinary practice, either from extraneous sources or by modifications of that practice.

That erroneous estimate has also given rise to much of the controversial opposition which **Liebig** has manifested towards the conclusions arrived at by the researches of **Lawes** and **Gilbert**, though virtually adopting those conclusions, and materially modifying his own views in accordance with them. It has also led him to imagine that the general doctrine of plant-nutrition has been called in question. But that is not the case; nor has this general doctrine ever been disputed, except in so far as relates to that extreme form of it, adopted by **Liebig**, according to which carbonic acid, water, and ammonia are held to be the only sources of the organic constituents of plants. (**Saussure**—1841—"Sur la Nutrition des Végétaux."—*Bibl. univ.* xxxvi. 340.—**Berzelius**—1842—*Jahresbericht*, xxii. 220.—**Mulder**, *op. cit.*—**Mohl**, *op. cit.* p. 78.) The originality of that extreme view was, indeed, disputed by **Dumas**, by whom it was also put forward about the same time. (**Dumas**—1841—"Sur le Rôle que joue l'air atmosphérique dans la nature, et sur l'action qu'il exerce sur tous les êtres organisés." *Rev. scient. indust.* vi. 228, and *Chemical and Physiological Balance of Organic Nature.*) **Berzelius**, in criticising that doctrine, remarked that, while it was still unsupported by any experimental evidence, it was so opposed to general agricultural experience, that it could not even be regarded as probable; though it manifested much genius and inspiration, and had been propounded with the art peculiar to **Dumas**, but less calculated, by soundness of argument, to overcome the doubts of those acquainted with the subject, than to impress others, less cognisant of it, by striking manner and positive assertion—the most efficient means of making precipitate scientific conclusions generally popular (*Jahresbericht*, xxii. 220). In reference to **Liebig's** views on the chemistry of agriculture, he also remarked that the mode in which he had sought to decide questions of the highest importance for that art, had met with greater recognition, as being perfectly trustworthy, than was consistent with the state of knowledge at that time. Of **Boussingault**, on the contrary, who had followed "the difficult and laborious course of deciding every question by experiment," he remarked, that "his answers, though not so rapid, were mostly trustworthy." (*Jahresbericht*, xxi. 236, 238.)

The difference thus early recognised by **Berzelius** between **Liebig's** mineral theory of agriculture, and **Boussingault's** views on the same subject, has been fully confirmed by the results of experience. The former may be looked upon as a thing of the past, the error of which has been demonstrated by the entire failure of the attempts to carry into practice its fundamental principle as to fertility and manure. The latter, though modified in some particulars by their development, and by the progress of research, have been found in the main correct, and are supported by the extended results obtained by **Lawes** and **Gilbert**, in the series of experiments they have conducted upon a working scale, during the last twenty years, with a strict regard to actual practice in the field, and in the laboratory, with all the refinement of modern methods of research.

The difference between Liebig's doctrine and the conclusions arrived at by Lawes and Gilbert, as the result of their experimental researches, does not relate to the abstract theory of plant-nutrition; but it relates solely to the ordinary system of agricultural practice, and chiefly to that branch of the "mineral theory" of agriculture propounded by Liebig, which comprises the principles of manuring. Liebig ascribed fertility and the efficacy of manure, solely to the amount of available ash-constituents in land, and the advantages of rotation, mainly to the unequal requirements of different plants for those substances.

Lawes and Gilbert, on the contrary, have shown that fertility is not proportionate to the amount of available ash-constituents in land; that the efficacy of manure is not proportionate to the amount of ash-constituents it contains; that the exhaustion of land, in the ordinary practice of agriculture, consists chiefly in a deficiency of nitrogenous food-material; that the advantage of rotation consists more in the accumulation of nitrogenous and carbonaceous food-materials in the farmyard manure, than in the difference between the ash-constituents taken from land by corn and fallow-crops; and that the requirements of cultivated plants cannot be measured merely by the results of their analyses.

The sterling value of the results thus obtained is not overrated by the opinion expressed in the annual address of the President of the Royal Agricultural Society of England, that "during the last twenty-five years, there has not been any addition made to our knowledge, which approaches, in importance, to the insight into the true principles of cropping and manuring, obtained on the experimental farm at Rothamsted." (**Thompson**—1864—*Journ. Roy. Agric. Soc.* xxv. 4.)

The particular conclusions and general views which have been arrived at by these researches have been vehemently disputed by **Liebig**, who has sought to maintain that they are at once totally erroneous, and perfectly confirmatory of his "mineral theory of agriculture." (**Liebig**—1851—*Letters on Chemistry*, 3rd edit.; 1855—*Principles of Agric. Chemistry*; 1863—*Natural Laws of Husbandry, Einleitung*, &c.—**Hofmann**, *Op. cit.* p. 160.)

This paradoxical position has been arrived at by a singular process.

It is contended that the "mineral theory" of agriculture comprised ammonia and its salts, among the mineral substances which were considered to determine the fertility of land and the efficacy of manure, and which it was, consequently, necessary to return or supply to land, in order to maintain or increase fertility. (**Liebig**—1855—*Principles of Agric. Chemistry*, p. 90.)

This claim, however, is quite inconsistent with **Liebig's** original exposition of his views, and with the pointed antithesis constantly maintained in all his writings, between the atmospheric food of plants, carbonic acid, water, and ammonia, whether furnished directly by the atmosphere, or indirectly from within the soil; and those materials derived exclusively from the soil, which "are mineral substances, and as such are indestructible by fire, and, consequently, remain as ashes after the incineration of the plants, or of their parts." It is also inconsistent with the general interpretation of his "mineral theory" by other writers on the subject. (See **Horsford**—1846—*Genesee Farmer*, Aug. 1855.—**Weissenborn**—1847—*Farmer's Magazine*.—**Schultze**—1848, *American Patent Office Report*, 1849.—**Johnston**—1848—*Jour. Roy. Agric. Soc. Eng.*, ix. 223.—**Puvis**—1844—*Traité des Amendments*, pp. 423, 623, 624, 627, 632.—**Boussingault**—1851—*Economie Rurale*, ii. 81.—*North British Agriculturist*, Nov. 7, 1855.) Moreover, it is certain that, in the specification of the patent which was the embodiment of Liebig's "mineral theory" in relation to practical agriculture, neither ammonia nor its salts were included* among the mineral substances mentioned in the recipes and directions given by him for the preparation of manures (see p. 845). In the "*Address*" also, though ammonia was stated to have been added to the manure in the first year, still the prospect of being able to exclude it altogether was spoken of as probable; and in the third edition of the *Letters on Chemistry*, 1851, (p. 502), a whole letter was devoted to the argument, that an artificial supply of nitrogen was quite a matter of indifference (p. 515); for though such a supply would exercise a favourable effect on vegetation, still, if it were not given, all the requisite nitrogen would be obtained from the atmosphere. (p. 518. See also *Allgemeine Zeitung*—1857—No. 157.)

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* The quantity of ammonia, amounting to less than 0·5 per cent., corresponding to the ammonio-magnesian phosphate in the manure, is of course considered as unimportant.

In the criticism of Lawes' and Gilbert's experiments and conclusions, Liebig has assumed that they have regarded certain substances as having a specific value as materials of plant-food in an abstract point of view; but this assumption is unfounded. Their experiments have only led them to consider that in a practical point of view, and in relation to the existing practice of agriculture, in this country especially, those materials of plant-food acquire a preponderating value as manure, which, like ammonia in the case of corn, become relatively deficient; or which are capable of determining a particular mode of growth, like phosphoric acid in the case of root-crops; that they are the materials to be supplied artificially, not with the object of wasting the available resources of land, but in order to prevent these from lying idle.

Herein lies a difference which Liebig has either failed to perceive, or studiously disregarded; and it is a difference of the highest importance. The practical farmer accepts, in its full significance, the abstract theory of plant-nutrition, so far as it concerns him: he also looks for its application to the art in which he is engaged, and for rules by which his practice may be improved. There is probably no art in which suggestions for improvement have been more eagerly accepted during the past twenty or thirty years than in agriculture; but when such suggestions are tested and found wanting, the practical nature of agriculture demands their abandonment.

So it has proved with Liebig's application of his theory of plant-nutrition to agriculture. Looking only to the ash-constituents of plants, of soils, and of manure, he has laid down rules for agricultural practice—he has prescribed manures, and written elaborate expositions of the various operations of culture, which in every single instance failed to bear the test of experience.

But where the enquiry into this subject has been conducted in a more catholic spirit, and by a method at once more philosophical and more directly relating to the ruling conditions of practical agriculture, as in the experiments of Boussingault, and of Lawes and Gilbert, the results obtained are calculated to afford materials for a legitimate induction, by which principles of real value in relation to the practice of the art may be arrived at.

The customary routine of agricultural practice, however defective it may be in particular cases, has become established by observation and experience, and by the exercise of the same mental functions which are employed in scientific research. Though their exercise may be limited by the practical object in view, there can be no doubt that, in reality, agricultural customs represent natural facts to a greater extent than science is yet competent to explain. To those who do not, like Liebig, consider the farmer to be "destitute of all understanding," the prejudices characteristic even of the rudest practice will, therefore, appear as the exponents of those peculiarities of climate, soil, and other circumstances, which lie at the root of the practice adopted. However vague and unintelligible such prejudices and empirical rules may appear, it is from the consideration of them, that a clue may be obtained to the scientific elucidation and improvement of agriculture. The science which is to be of value in agriculture, and whose value will be recognised by farmers, must grow out of the practice of the art, and the patient examination of its various details, and not be a mere speculative grafting upon it. The accumulated data of ordinary experience must furnish the basis for its construction, and its doctrines must rest upon evidence of reality, not upon mere probability. It may be a slow growth, but it must be a sure one.

Meanwhile, it is no reproach to the farmer if he adheres to the system which he knows by experience to have brought him certain results, or that he refuses to adopt another system until he has sufficient proof of its being more advantageous than that with which he is familiar. This natural conservative tendency has been strengthened by the failures attending the premature application of scientific doctrines. This is really the reason why farmers are in many cases averse to the adoption of improvements suggested by science. It is not because they are "destitute of all understanding," or because they pretend to deny the existence of any connection between scientific doctrines and the phenomena concerned in agriculture, but because it is still questionable whether those doctrines really furnish the means of improvement. For this reason they prefer to be guided by tradition and experience, rather than by untried precepts of scientific speculation. If there be an established and invariable connection between the practice of rotation with cattle-feeding, and the profitable result of farming—

between the use of superphosphates and the production of a large root-crop—between the use of nitrogenous manure and the increase of corn-crops—those practices will continue to be adopted, and they will constitute the scientific practice of agriculture, quite independent of the questions whether superphosphate or ammonia have any special value as materials of plant-food, or what becomes of those portions of them which are supplied as manure and are not obtained in the crop. These are abstract scientific questions of high interest for the chemist, and of possible importance to the future of agriculture; but they do not concern the farmer, whose business is to produce food with such means as are at his disposal. It would be a very illogical conclusion that the facts observed as to the influence of artificial supplies of ammonia and superphosphates upon the growth of corn- and root-crops should be disregarded because science is unable to explain the precise functions of those substances in vegetation; and it is equally irrational to denounce, as a folly and an error, the application of those facts so far as present knowledge will admit. B. H. P.

MARASMOLITE. Syn. with Blende. (See Zinc, Sulphide of.)

MARBLE. See Limestone (p. 697).—Church (Chem. Soc. J. xvii. 379) has lately examined the colouring matter of the Blue Forest Marble, and has shown that the colouring material of the dark bands which occupy the central portion of the various-sized slabs into which the stone has naturally divided, consists of iron pyrites, while the paler yellow, brown, or buff tint of the outer parts of the slabs is due to ferric oxide resulting from the oxidation of the pyrites. It appears probable that the colouring of other blue and grey clays, rocks, and soils may also be due to the presence of iron pyrites; and hence, perhaps, may be explained the injurious influence which these blue and grey matters exert on vegetation.

MARCASITE. White iron pyrites. (See Iron, Sulphides of, p. 402.)

MARCELINE. A name applied to an impure variety of braunite (manganic oxide); also used as a synonym of rhodonite (silicate of manganese).

MARCYLITE. A mineral having the aspect of tenorite cupric oxide), from the southern part of Red River, in the neighbourhood of Mount Witchita. Hardness = 3. Specific gravity = 4·0 to 4·1. In the flame of a candle it melts, and acquires a blue or green colour. On charcoal it gives off vapours of chloride of copper, and ultimately leaves pure copper. In the pulverised state, it dissolves completely in ammonia. Contains 54·3 per cent. copper, 36·2 chlorine and oxygen, and 9·5 water. (C. U. Shepard, Sill. Am. J. [2] xxi. 206.)

MARECANITE. Syn. with Pearlstone.

MARGARIC ACID. $C^{17}H^{34}O^2 = \left.\begin{matrix}C^{17}H^{33}O\\H\end{matrix}\right\}O$. (Heintz, Pogg. Ann. cii. 272.)—This term was formerly applied to an acid intermediate between stearic and palmitic acids, supposed to be produced, together with others, by the saponification of solid natural fats; but it is now restricted, for reasons presently to be mentioned, to an artificially prepared fatty acid of the series $C^nH^{2n}O^2$, resulting from a definite reaction.

a. *Artificial Margaric acid.*—This acid is produced by the action of potash on cyanide of cetyl (margaronitrile):

$$C^{17}H^{33}N + 2H^2O = C^{17}H^{34}O^2 + NH^3.$$

Cyanide of cetyl (oily, see i. 841) is continuously boiled with alcoholic potash, till ammonia is no longer given off, and the residue has become solid; this residue is then decomposed by boiling dilute hydrochloric acid; the separated fatty acid is shaken up with aqueous ammonia; and the turbid solution is precipitated by chloride of barium. The precipitate, after being washed with water and with alcohol, and repeatedly boiled with ether, yields to this solvent an oil, which solidifies in the cold, melts below 40°, and has the composition of a mixture of cetylic ether and cetylic aldehyde. The undissolved barium-salt is decomposed by agitation with hydrochloric acid and ether; and by pipetting off the ethereal liquid, and distilling off the ether, crude yellowish margaric acid is obtained, melting at 56·6°, and solidifying in scales and fine needles. This acid may be resolved, by several crystallisations from alcohol, repeated partial precipitation from the solution of its sodium-salt by acetate of magnesium, and subsequent recrystallisation of the portions of acid again separated (somewhat in the manner described on page 474) into margaric acid, and an acid containing a larger proportion of carbon ($C^{19}H^{38}O^2$, formed from cyanide of *stethyl*, $C^{19}H^{37}N$, contained in the cyanide of cetyl employed), which occurs chiefly in the portions first precipitated by acetate of magnesium. (Heintz.)

The portions last precipitated by acetate of magnesium yield margaric acid, which, after its melting-point has been raised by repeated crystallisation to 59·9°, exhibits the characteristics of a pure fatty acid mentioned below, and cannot in any way be resolved into acids differing in melting-point. This is the only way in which pure margaric acid can be obtained. The acids formerly so called, obtained by the saponification of natural fats, were mixtures of stearic acid with palmitic acid, or other acids of lower melting-point.

Margaric acid forms white crystals, melting at 59·9°, and solidifying in crystalline scales on cooling. It contains, according to the mean of Heintz's analyses, 75·45 to 75·55 per cent. carbon, and 12·51 to 12·57 hydrogen; the formula requiring 75·56 carbon, 12·59 hydrogen, and 11·85 oxygen.

But few of the margarates have been prepared. The *barium-salt*, $C^{17}H^{33}BaO^2$, obtained by precipitating the sodium-salt with nitrate of barium, and washing with water, is a white amorphous powder yielding, by analysis, 60·39 per cent. C, 9·80 H, and 22·40 Ba^2O; the formula requiring 60·44 C, 9·78 H, and 22·67 Ba^2O.

The *silver-salt*, $C^{17}H^{33}AgO^2$, obtained in like manner by precipitation, dries up to a loose, white, amorphous powder, containing 53·67 per cent. C, 8·74 H, and 28·85 Ag (calc. 54·11 C, 8·75 H, 28·65 Ag, and 8·74 O).

The *sodium-salt* is prepared by adding a boiling aqueous solution of pure sodic carbonate to a boiling alcoholic solution of margaric acid, evaporating to dryness over the water-bath, exhausting the residue with boiling alcohol, and filtering hot. The filtrate, which solidifies to a jelly on cooling, is liquefied by heat and mixed with water in the proportion of one-eighth of the volume of the alcohol employed, whereby a mother-liquid is formed which takes up any foreign salts present. On again solidifying, the salt is collected on linen and strongly pressed.

β. The *so-called* margaric acid *obtained by saponification of natural fats.*—Chevreul in 1820 distinguished the solid acids resulting from the saponification of fats, as margaric acid and margarous, afterwards stearic acid; the former melting at 60°, the latter at 75°, and solidifying at 70°. He did not consider the difference between the two acids to be fully established, but suggested that margaric acid might be a mixture of stearic acid with another acid more fusible and richer in oxygen.

The fatty acid melting at 60° was, however, afterwards examined by several chemists (see Gerhardt, *Traité*, ii. 835), and regarded as a separate acid, having the composition $C^{17}H^{34}O^2$; and this view of its nature continued to prevail, till Heintz, in a series of researches published in 1852 and subsequent years, showed that it was not a distinct acid, but could be separated, by certain processes, into stearic acid and other fatty acids of lower melting-point. The leading points established by Heintz in this series of researches (for the references to which see *Gmelin's Handbook*, xvi. 343, 344), are the following:

1. All the acids obtained in the saponification of fats contain an even number of carbon-atoms (C = 12).
2. The margaric acid of most chemists is separable into palmitic and stearic acids.
3. Fatty acids may be mixtures, and not definite compounds, even though neither their composition nor their melting-point can be altered by recrystallisation.
4. Such mixtures may, however, be separated by partial precipitation (p. 474).
5. They differ from pure acids as regards their melting-point and their mode of solidifying.

Heintz has, moreover, determined with accuracy the melting-point, composition, and many other properties of the fatty acids, and has also drawn up tables, hereafter to be given, of mixtures of fatty acids of known composition (see MYRISTIC, PALMITIC, and STEARIC ACIDS). From these, and the investigations of other chemists subsequently published, it appears that the nature of the bodies described as margaric acid is probably as follows:

a. Margaric acid of Chevreul.—This, according to Heintz, is to be regarded as a mixture of about 90 per cent. palmitic acid and 10 per cent. stearic acid, which is probable from the circumstance that it crystallises in needles on cooling. Of similar nature are doubtless the margaric acid of Varrentrapp (Ann. Ch. Pharm. xxxv. 84), obtained from human fat; that from goose-fat by Gottlieb (*ibid.* lvii. 56); from shea-butter by Thomson and Wood (J. pr. Chem. xlvii. 237), and many others.

b. Margaric acid of Bromeis.—The acid obtained by oxidation of stearic acid is undecomposed stearic acid, which owes its lower melting-point to association with volatile acids (see STEARIC ACID).—Respecting the margaric acid which Bromeis (Ann. Ch. Pharm. xxxv. 93) obtained from impure oleic acid by the action of nitric acid, see OLEIC ACID.

c. Margaric acid of Redtenbacher and Varrentrapp.—That of Redtenbacher is obtained by the dry distillation of stearic acid, when, according to Heintz, most of the stearic acid passes over unchanged. That of Varrentrapp (Ann. Ch. Pharm. xxxv. 65), obtained by the dry distillation of beef-suet, hog's-lard, olive-oil, or crude oleic acid, doubtless varies in composition according to the kind of fat employed.

d. Anderson's *Margaric acid* (Ann. Ch. Pharm. lxiii. 376) is obtained, together with sulphydric acid, odmyl, and other products, by the dry distillation of almond-oil with sulphur. It contains, on the average, 75·34 per cent. C, 12·58 H; in the silver-salt, 28·62 per cent. silver; in the ethylic ether, 76·33 per cent. C, 12·73 H, and 10.97 O. It appears to be palmitic acid formed by the decomposition of oleic acid.

e. Margaric acid of Poleck, Lewy, and others, obtained by the dry distillation or saponification of wax, is doubtless palmitic acid, more or less pure.

MARGARIC ETHERS. No compounds of the alcohol-radicles with pure margaric acid (Heintz's), have yet been obtained. The compounds to which the name has generally been applied were probably mixtures of stearic and palmitic ethers. A similar remark applies to Chevreul's *margarin.*

MARGARITE. *Perlglimmer, Emeryllite, Corundellite,* and *Clingmannite.*— A silicate of calcium and aluminium, occurring in trimetric hemihedral crystals, with a monoclinic aspect, like muscovite; tabular from predominance of the form oP. Angle ∞P : ∞P = 119° to 120°. Lateral planes longitudinally striated. Cleavage basal, eminent. Usually in intersecting or aggregated laminæ, sometimes compact, massive, with a somewhat scaly structure. Hardness = 3·5 to 4·5. Specific gravity = 3·032 to 2·99: the latter for margarite (Hermann), 2·995 for emeryllite (Silliman, jun.). Lustre of base pearly, laterally vitreous. Colour greyish, reddish, or yellowish. Translucent to subtranslucent. Laminæ rather brittle.

Analyses.—a. From Sterzing, in the Tyrol (Smith and Brush, Sill. Am. J. ii. xv. 209). *b.* From the corundum mines of Gumuchdagh, in Asia Minor. *c.* From the island of Nicaria, in the Grecian Archipelago. *d.* From Naxos. *e.* From Katharinenburg, in the Ural (J. L. Smith, *ibid.* xi. 59 and xv. 208). *f.* From Village Green, Chester county, Pennsylvania (Craw, *ibid.* viii. 379). *g.* From Buncombe county, North Carolina (B. Silliman, *ibid.* viii. 1). *h.* From Unionville, Pennsylvania (Craw, *loc. cit.*:

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Silica . . .	28·55	30·83	30·04	29·68	28·50	31·20	29·17	29·99
Alumina . . .	50·24	49·30	49·08	49·38	51·02	50·86	48·40	50·57
Ferric oxide . .	1·65	2·03	1·48	1·26	1·78			
Lime . . .	11·88	10·83	11·20	11·18	12·05	10·25	9·87	11·31
Magnesia . . .	0·69	0·50	trace	. .	. .	0·45	1·24	0·62
Soda and potash .	1·87	1·90	2·58	1·25	?	2·29	6·15	2·47
Water . . .	4·88	3·88	4·72	5·05	5·04	4·83	3·99	5·14
Fluorine . . .	. .	. .	. .	. .	. .	. .	2·00	
	99·76	99·27	99·10	97·80	98·39	99·88	100·82	100·10

These analyses lead to the formula $Ca^2O.2Al^4O^3.2SiO^2.H^2O$ (the calcium being partly replaced by potassium and sodium, and the aluminium by ferricum).

Corundellite is margarite from Unionville, Chester county, Pennsylvania. *Clingmannite* is the same mineral from Buncombe county, North Carolina.

Diphanite (ii. 430) is also a variety of margarite. (Dana, ii. 300. Rammelsberg's *Mineralchemie*, p. 843.)

MARGARODITE. A variety of muscovite or biaxial mica, apparently formed from that mineral by assumption of water, and loss of alkalis and ferric oxide. A specimen from Monroe, Connecticut, analysed by Smith and Brush (Sill. Am. J. [2] xvi. 46), gave by analysis 46·50 per cent. silica, 33·91 alumina, 2·69 ferric oxide, 0·90 magnesia, 2·70 soda, 7·32 potash, and 4·63 water, with 0·82 fluorine and 0·31 chlorine.

MARGARONE. The acetone of margaric acid: it has not been prepared from the pure acid.

MARIALITE. Syn. with HAUYNE (p. 14).

MARIONITE. A hydrous carbonate of zinc, containing 73·26 per cent. Zn^2O, 15·01 CO^2, and 11·81 water, found in Marion county, Arkansas (Elderhorst, Sill. Am. J. [2] xxix. 383). A mineral of the same composition occurs at Cumillas, near Santander, in Spain. Its composition is expressed nearly by the formula:

$$8Zn^2O.3CO^2.6H^2O, \text{ or } 3Zn^2CO^3.5Zn^2O.6H^2O.$$

(Petersen and Voit, Jahresb. 1858, p. 734.)

MARINE METAL. An alloy introduced by Wetterstedt in 1833, for the sheathing of ships. It consists of 94·4 per cent. lead, 4·3 antimony, and 1·3 mercury; has a specific gravity of 11·1, is very malleable, but harder than lead. It is said not to be attacked by water or hydrochloric acid, and to be twice as cheap as copper. It does not appear, however, to have been practically used.

MARIOTTE'S LAW. The law which expresses the inverse proportionality of the volume of a gas, to the pressure to which it is subjected at a given temperature. (See ii. 370, 819.)

MARJORAM, OIL OF. The volatile oil obtained by distilling sweet marjoram (*Marjorana hortensis* or *Origanum marjorana*) with water is lighter than water, and contains a considerable quantity of camphor or stearoptene. When freed from the latter by rectification, it boils at about 161°, and appears to have the composition of oil of turpentine, containing, according to Kane (Ann. Ch. Pharm. xxxii. 285), 86·7 to 86·1 per cent. carbon, 11·1 to 11·4 hydrogen, and about 2 per cent. oxygen, probably arising from a small quantity of the camphor not completely separated.

The camphor of marjoram is hard, colourless, inodorous, heavier than water, melts when heated, and sublimes without residue. It is soluble in boiling water, in ether, nitric acid, and sulphuric acid, the last colouring it red. It contains, according to Mulder (Ann. Ch. Pharm. xxxi. 69), 60·0 per cent. carbon, and 10·7 hydrogen.

MARL. See LIMESTONE (p. 698).

MARMATITE. A black ferruginous variety of blende, found at Marmato, near Popayan, South America. (See ZINC, SULPHIDE OF.)

MARMOLITE. Syn. with SERPENTINE.

MARRUBIÏN. (Kromayer, Arch. Pharm. [2] cviii. 257.)—The bitter principle of white horehound (*Marrubium vulgare*). To prepare it, the dried herb is repeatedly exhausted with hot water; the united and concentrated extracts are treated with recently-ignited animal charcoal; and the charcoal, after washing with water, is well boiled with alcohol, whereby a bitter solution is obtained, which, when freed from the greater part of the alcohol by distillation, and then left to evaporate, deposits crude marrubiïn as a brown bitter balsam. For purification, it is dissolved in alcohol; the solution is mixed with water till it begins to show turbidity, then with acetate of lead; and the filtered liquid, after being freed from lead by sulphydric acid, is left to evaporate. The marrubiïn then separates in light brownish-yellow oily drops, which, when separated from the mother-liquid, solidify in crystalline masses. Only a part of the marrubiïn, however, assumes the crystalline form; the rest, which in other respects, resembles the crystallised substance, solidifying in the amorphous state. In preparing marrubiïn also from fresh horehound, the greater part of the product is obtained in the amorphous state.

Marrubiïn crystallises from ether in colourless rhombic plates, or thick four-sided twin-crystals; from alcohol in needles. It is nearly insoluble in cold *water* (whence the bitter taste of horehound becomes perceptible after some time only); somewhat more soluble in hot water. *Alcohol* and *ether* dissolve it readily, forming perfectly neutral solutions. Marrubiïn melts at 160°, and solidifies crystalline on cooling; at higher temperatures, it gives off white, very irritating vapours. When heated in a test-tube, it distils in oily drops, giving off pungent vapours smelling like oil of mustard. Strong *sulphuric acid* dissolves it with brown-yellow colour: strong *hydrochloric acid* does not act upon it even when heated; strong *nitric acid* does not act on it in the cold, but dissolves it with yellow colour when heated. It is not perceptibly altered by *alkalis*, or by *metallic salts*, and produces but a slight reduction in ammoniacal nitrate of silver; neither is it precipitated by *tannic acid*.

MARSH-GAS.—*Light carburetted* hydrogen, *Hydride of Methyl*, CH^4.

This hydrocarbon gas is very abundant in nature. The bubbles of gas which are so often seen on the surface of stagnant water consist of it, mixed with nitrogen and carbonic acid. From its occurrence in this way in marshy districts it takes its name. Great quantities of it are given off by many of the coal-beds, so that it often accumulates in coal pits, where it is known as the *fire-damp* of the miners, and is the cause of the explosions which occur in those places. It is, moreover, found escaping from the earth in many parts of Italy, Persia, China, and America.

Besides being one of the usual products of the decay of organic substances, and also of their destructive distillation, especially when this operation is performed at elevated temperatures, and in general of the imperfect combustion of fuel, it constitutes a large proportion of common illuminating gas. Bunsen's analysis of Manchester coal gas gives 34·90 vols. of marsh-gas in every 100 vols. of the gas.

In the laboratory—if we except this production of it by the imperfect combustion or destructive distillation of organic substances—it is comparatively a rare product. The prinicipal other reactions which are known to yield it are:—

(1) The action of nascent hydrogen on tetrachloride of carbon (the nascent hydrogen being generated by the action of potassium-amalgam on water.) (Regnault.)

$$CCl^4 + H^8 = CH^4 + 4HCl.$$

(2) The action of zinc-methyl on water, and certain analogous actions of the same kind. (Frankland.)

$$CH^3Zn + H^2O = CH^3H + ZnHO.$$

From this reaction it derives its name, hydride of methyl.

(3) The action of sodium on iodide of methyl in presence of ether (Wanklyn and

Buckeisen), which, instead of yielding pure methyl, gives a large quantity of hydride of methyl.

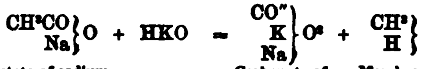
(4) The action of sulphide of carbon upon sulphuretted hydrogen and copper, or iron at a red heat; also the action of sulphide of carbon on phosphoretted hydrogen and copper. (Berthelot.)

There is also some reason for believing that it is produced by the direct action of hydrogen on carbonic anhydride at a red heat, since when marble is heated in a current of hydrogen, more water is generated than corresponds to the simple reduction of the carbonic acid to carbonic oxide. (Wanklyn and Frank.)

Preparation.—The readiest way of preparing large quantities of marsh-gas in a state of tolerable purity is by the destructive distillation of a mixture of an alkaline acetate with a hydrated alkali.

It is recommended to employ 2 parts of crystallised acetate of sodium, 2 parts of caustic potash, and 3 parts of powdered quicklime (Dumas, Ann. Ch. Phys. [2] lxxiii. 92). The object of using the quicklime is to save the retort, which might otherwise be perforated by the caustic potash. In conducting the operation, a little caution is requisite; no trace of gas comes off until the temperature is very high, and then there is a sudden rush of gas.

The reaction between the alkali and the acetate is tolerably precise:



$$\underset{\text{Acetate of sodium.}}{\left.\begin{matrix}CH^3CO\\Na\end{matrix}\right\}O} + HKO = \underset{\text{Carbonate of potassium and sodium.}}{\left.\begin{matrix}CO''\\K\\Na\end{matrix}\right\}O^3} + \underset{\text{Marsh-gas.}}{\left.\begin{matrix}CH^3\\H\end{matrix}\right\}}$$

With the exception of Bunsen's destructive distillation of cacodyl,

$$\underset{\text{Cacodyl.}}{2As(CH^3)^2} = As^2 + \underset{\text{Marsh-gas.}}{2CH^4} + \underset{\text{Ethylene.}}{C^2H^4},$$

it is the only destructive distillation which yields marsh-gas by a precise reaction.

Marsh-gas prepared as just described from the acetate is, however, liable to certain small quantities of impurity. It is easy to see how small quantities of acetone-vapour are almost inevitable: for destructive distillation of an acetate alone gives acetone.

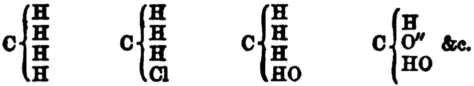
If marsh-gas of a high degree of purity be required, it may be obtained by decomposing zinc-methyl with water.

Of all known compounds, marsh-gas is the richest in hydrogen, containing as much as 25 per cent. Next to hydrogen itself it is the lightest gas (specific gravity 0·5576), and is thence not inappropriately named *light carburetted hydrogen*. In general character it bears a great resemblance to hydrogen. It is incondensable, colourless, without taste or smell; neutral to test-paper, and very neutral altogether. It is distinguishable from all other hydrocarbons by the low luminosity of its flame. In *water* and in *alcohol* it is very sparingly soluble. 100 vols. of water at 0° C. dissolve 5·449 vols. of marsh-gas; 100 vols. of alcohol at 0° C. dissolve 52·259 vols. (Bunsen). The sparing solubility of marsh-gas in alcohol affords a method of separating it from some other hydrocarbon gases, such as ethyl, which dissolve in alcohol to a much greater extent. By means of *sulphuric acid* or *bromine* (neither of which attacks it), the olefines may be removed from a gaseous mixture containing marsh-gas and olefines. It is not absorbed by potash, and indeed there is no reagent which absorbs it. From acetylene it is easily separated by means of an ammoniacal solution of *cuprous chloride*. The same reagent, or the hydrochloric solution of cuprous chloride, might be employed to remove carbonic oxide (see ANALYSIS OF GASES, i. 283). According to Dumas, it is not attacked by *chloride of sulphur*, nor by *pentachloride of phosphorus*, nor by *pentachloride of antimony*. According to Kolbe, a hot and concentrated mixture of *sulphuric and nitric acids* does not affect it. In the dark, dry *chlorine* is without action upon it. A mixture of 2 vols. of chlorine with 1 vol. of marsh-gas is not at first visibly affected by sunlight, but after a while it explodes. The passage of an electric spark also determines an explosion. If the gaseous mixture be diluted with carbonic anhydride, and then exposed to sunlight, a quiet chlorination takes place; and if excess of chlorine be there, chloroform and tetrachloride of carbon are produced (Dumas). Equal volumes of dry chlorine and marsh-gas exposed to diffused daylight, give a chlorinated product, having the formula CH^3Cl. It appears that this compound, CH^3Cl, if not identical with chloride of methyl, is very readily converted into it: for Berthelot has succeeded in obtaining methyl-compounds from it by double decomposition.

If moisture be present, chlorine converts marsh-gas into hydrochloric acid, carbonic acid, and carbonic oxide.

At a white heat, marsh-gas is resolved into carbon and hydrogen. The same change is effected by the transmission of electric sparks, but the decomposition is never complete.

Carbon being a tetratomic element, marsh-gas is the normal hydride of carbon, and the type of a numerous class of compounds which are produced by replacement of more or less hydrogen by other radicles. Thus chloride of methyl is monochlorinated marsh-gas: Methyl-alcohol is marsh-gas wherein hydrogen has been replaced by peroxide of hydrogen: Formic acid is marsh-gas wherein some of the hydrogen has been replaced by oxygen and some by peroxide of hydrogen, *e.g.*—



$$C\begin{cases}H\\H\\H\\H\end{cases}\qquad C\begin{cases}H\\H\\H\\Cl\end{cases}\qquad C\begin{cases}H\\H\\H\\HO\end{cases}\qquad C\begin{cases}H\\O''\\HO\end{cases}\quad \&c.$$

Marsh Gas. Chloride of Methyl. Methylic Alcohol. Formic Acid.

When carbon makes a partial saturation of itself, as polyatomic elements occasionally do, and as carbon of all polyatomic elements is especially liable to do, there result complex carbon-groups requiring very various amounts of hydrogen for their saturation. When the carbon has adhered to itself with the least possible expenditure of saturating power, and when the complex carbon-group so resulting is fully saturated with hydrogen, there result certain hydrocarbons which form a very well characterised family—the marsh-gas family. The marsh-gases—homologues of marsh-gas—are characterised by their great neutrality, and present a uniformity of character which is most remarkable. J. A. W.

MARSH'S TEST FOR ARSENIC. See ARSENIC (i. 362).

MARTINSITE. A variety of common salt from Stassfurth, containing 10 pts. chloride of sodium to 1 pt. sulphate of magnesium. (Karsten, J. pr. Chem. xxxvi. 127.)

MARTITE. The octahedral form of native ferric oxide, found on the Puy de Dome; at Tramont; in Monroe County, New York; in Peru; and in Brazil. The crystals are regular octahedrons, often flattened, and having the octahedral faces striated parallel to the edges. Cleavage indistinct. Hardness = 6. Specific gravity = 4·82, Brazil; 4·65, Puy de Dome; 3·80, Peru (Breithaupt); 5·33, Monroe (Hunt). Lustre submetallic. Colour iron-black, sometimes with a bronze tarnish. Streak brown, or purplish-brown. Fracture conchoïdal. Not magnetic.

MARTYLAMINE. Syn. with XENYLAMINE.

MARUM-CAMPHOR. A camphor or stearoptene existing in all parts of cat-thyme (*Teucrium Marum*). It is extracted by distilling the dry herb with water, and repeatedly cohobating the distillate over fresh quantities of the green herb. It is a white, crystalline, transparent, brittle mass, consisting of thin laminæ, heavier than water, having an unpleasant odour and aromatic taste. (Bley, N. Trommsd. xiv. 2 and 87.)

MASCAGNINE. A sulphate of ammonium, $(NH^4)^2SO^4.2H^2O$, occurring about volcanoes; it was discovered by Mascagni in the fissures of the lava at Etna, Vesuvius, and the Lipari Isles. It sometimes forms trimetric crystals in which $a:b:c = 0·731 : 1 : 1·129$. Angle $\infty P : \infty P = 107° 40'$; $oP : \breve{P}\infty = 122° 56'$. Cleavage, perfect parallel to $\infty\breve{P}\infty$; imperfect parallel to oP. Usually in mealy crusts and stalactitic forms. Hardness = 2·25. Specific gravity = 1·72 to 1·73. Lustre when crystallised vitreous. Colour yellowish-grey to lemon-yellow. Translucent. Tastes pungent and bitter. (Dana, ii. 379.)

MASOPIN. $C^{12}H^{18}O^2$. (Genth, Ann. Ch. Pharm. xlvi. 124.)—A resinous substance obtained from a material used in Mexico for chewing. This latter substance, which is said to be derived from a tree called *Dschilte*, growing abundantly in Mexico, forms crude porous lumps having a dull aspect, but presenting a bright surface when cut; it softens between the fingers, has little or no taste when chewed, but a distinct odour like that of rotten cheese. To extract the masopin, the dried juice is comminuted and exhausted by boiling with water; and the soft ropy residue is digested with absolute alcohol, which on cooling deposits masopin in crystalline flocks, a further quantity separating on addition of water. The portion of the juice insoluble in alcohol consists of caoutchouc.

Masopin is a snow-white, light, pulverulent substance, which becomes adhesive when passed between the fingers, has neither smell nor taste, is insoluble in water, but easily soluble in alcohol and in ether, and crystallises from the ethereal solution in white silky needles or frequently in tufts of small prisms. The crystals melt at 155°, emitting an agreeable odour, and the melted mass solidifies on cooling to a glassy, brittle, yellow substance, having a conchoïdal fracture, and melting again at 69° or 70°.

Masopin yields by distillation a brown viscid oily mass, having an acid reaction. If the acid be removed by digestion with ammoniacal water, and the remainder then rectified over slaked lime, a light-yellow mobile oil is obtained, having an agreeable odour of ginger, and containing 88·02 per cent. carbon, and 11·49 hydrogen. The acid which unites with the ammonia separates, on addition of hydrochloric acid, in nacreous crystals like boracic acid: it may be further purified by precipitation from solution in potash. It forms a dazzling-white silver-salt, which burns with an odour of cinnamon, and contains 45·49 per cent. silver oxide.

Masopin dissolves gradually in nitric acid, and the solution leaves on evaporation a viscid mass like melted sugar, which is soluble in water, ammonia, and potash, and when combined with the latter, forms dingy yellow precipitates with most metallic salts.

MASSICOT. Protoxide of lead prepared without fusion. See LEAD, OXIDES OF (p. 549).

MASSOY-CAMPHOR AND OIL. Massoy-bark, obtained from New Guinea, and said to be the bark of *Laurus Burmanni*, or of *Cinnamomum Kiamis* (Nees), contains a camphor or stearoptene, and two volatile oils. The camphor is heavier than water, soluble in alcohol, ether, and acetic acid, and coloured yellow by nitric acid. The heavier of the two oils sinks in water, becomes pasty at 10°, has a pungent taste, and is coloured deep red by nitric acid. The lighter oil is more volatile, has a stronger odour like that of sassafras, is lighter than water, dissolves easily in alcohol, ether, and acetic acid, and is coloured cherry-red by nitric acid. The two oils and the camphor are obtained from the bark by distillation with water. (Bonastre, J. Pharm. xv. 204.)

MASTERWORT, OIL OF. (Wackenroder, Br. Arch. xxxvii. 341.—Hirzel, J. pr. Chem. xlvi. 202.)—The root of masterwort (*Imperatoria Ostruthium*) contains a volatile oil, which may be extracted by distilling the comminuted root with water. Part of it floats on the watery distillate; the rest may be obtained by agitation with ether and evaporation, and the whole purified by rectification with a small quantity of water and dehydration over chloride of calcium. The yield of oil is from 0·78 to 0·78 per cent.

This oil is transparent and colourless (Hirzel), pale yellow (Wackenroder), mobile (the portion which distils between 200° and 220° is more viscid). It boils between 170° and 220°; has an aromatic odour (somewhat empyreumatic, between 200° and 220° according to Hirzel); penetrating (Wackenroder); its taste is strongly heating (Hirzel); camphorous like that of poppy-oil (Wackenroder). It burns with a bright fuliginous flame.

The portion which distils between 170° and 180° contains, according to Hirzel, 85·57 per cent. carbon, 11·45 hydrogen, and 2·98 oxygen; that which distils between 200° and 220° contains 81·43 carbon, 11·32 hydrogen, and 7·25 oxygen. The oil appears to be a mixture of several hydrates of a hydrocarbon isomeric with oil of turpentine, corrresponding with the formula $4C^{10}H^{16}.H^2O$ and $3C^{10}H^{16}.2H^2O$. (Hirzel.)

It absorbs *chlorine*, with rise of temperature and evolution of hydrochloric acid gas, being thereby converted into a yellow viscid oil, which sinks in water, has a peculiar odour, and a biting taste. It is decomposed in like manner by *bromine*, with evolution of hydrobromic acid. By distillation with *phosphoric anhydride* it yields a transparent colourless oil, which has an odour of rosemary and an aromatic taste, and is isomeric with oil of turpentine. This latter oil absorbs hydrochloric acid gas, assuming a reddish-yellow colour, and forming, after complete saturation, rectification with water, and dehydration with chloride of calcium, an oil which has an agreeable odour, an aromatic taste, and a composition (74·98 C, 10·86 H, 13·28 Cl) agreeing with the formula $3C^{10}H^{16}.HCl$. (Hirzel.)

MASTIC. A resin obtained by incisions in the bark of the stem and branches of *Pistacia Lentiscus*, a tree growing in the islands of the Grecian Archipelago, especially in Chios. It forms small round transparent grains, having a faint agreeable odour, which becomes very distinct when the resin is thrown on red-hot coals. It softens when masticated, and is said to strength the gums. It is also used in fumigations, and in the composition of varnishes. Specific gravity = 1·074. According to Schrötter, its composition is $C^{20}H^{32}O^2$.

Aqueous alcohol dissolves the greater part of the resin, leaving masticin undissolved. The more soluble portion, which, according to Johnston, has the composition $C^{40}H^{32}O^4$, is precipitated from its solution by chlorine as a viscid mass. When heated for some time to 145° in the dry state, it is said to be resolved into two other resins, one containing a larger, the other a smaller proportion of oxygen.

MASTIC CEMENT. A building cement composed of finely-ground oolitic limestone mixed with sand and litharge, and made into a loosely coherent paste with linseed-oil. (See CEMENTS, i. 820.)

MASTICIN. $C^{40}H^{31}O^{2}$, according to Johnston.—The constituent of mastic resin which is the least soluble in alcohol, amounting to $\frac{1}{12} - \frac{1}{8}$ of the whole. It is white, soft at ordinary temperatures, but by prolonged drying and fusion becomes transparent, yellowish, and friable, and is said to be then more soluble in alcohol.

MATICIN. A bitter substance of unknown composition obtained from the leaves of the matico (*Piper asperifolium*), a plant growing in Peru. The leaves, which have a strongly aromatic and slightly astringent taste, are noted in Peru for their medicinal properties, and especially for their styptic power. When boiled with water, they yield a somewhat considerable quantity of a heavy volatile oil, while the maticin dissolves in the water, together with several other substances, from which it may be partly freed by precipitation with acetate of lead. The maticin then remains dissolved in the water, and may be obtained, by evaporation to a syrup, solution in alcohol, and evaporation of the alcoholic solution, as a yellow-brown extractive matter, having a disagreeable odour and extremely bitter taste. It is soluble in alcohol and in water, insoluble in ether. The aqueous solution is not precipitated by platinic chloride, but forms a yellow precipitate with potash, and with ammonia. (Hodges, Phil. Mag. [3] xxv. 204; Mem. Chem. Soc. i. 123.)

MATICO, OIL OF. To obtain this oil, the leaves of *Piper asperifolium* are distilled with water, and the oil which slowly sinks to the bottom of the milky distillate is collected. Pale green, thickish; has a strong and persistent odour, and a persistent camphorous taste. By keeping, it becomes thicker and ultimately crystalline; by nitric acid, it is coloured amber-yellow and resinised. It dissolves in oil of vitriol, forming a carmine-coloured liquid which becomes milky on addition of water. It dissolves readily in alcohol and ether, not in aqueous potash or ammonia. (Hodges, *loc. cit.*)

MATLOCKITE. Oxychloride of lead, $Pb^{4}Cl^{2}O$, found at Matlock in Derbyshire (p. 335).

MATRICARIA CHAMOMILLA. *Wild chamomile.*—The flowers of this plant distilled with water, yield a volatile oil of a dark blue colour, and nearly opaque, with a strong odour of chamomile, and an aromatic burning taste. It is fluid at 12°, but thickens when cooled below 0°. (*Gmelin's Handbook*, xiv. 365.)

MATRICARIA PARTHENIUM. *Feverfew.*—This plant, while in the flowering state, yields by distillation with water a greenish oil, which begins to pass over between 165° and 220°, the largest portion, however, distilling between 205° and 220°. The oil consists of a hydrocarbon containing about 86 per cent. carbon and 11 hydrogen, a camphor having the same composition as that of the lauraceæ, but possessing lævorotatory power (see CAMPHOR, i. 729), and an oxygenated oil containing more oxygen than camphor. (Dessaignes and Chautard, J. Pharm. xiii. 251.—Chautard, Compt. rend. xxxvii. 166.)

MAUILITE. Syn. with LABRADORITE (p. 450).

MAYNAS RESIN. *Calaba* or *Galba* of the Antilles (Lewy, Ann. Ch. Phys. [3] x. 380). A resin extracted by incision from *Calophyllum Calaba*, Jacq., a tree growing on the plains of San Martino and of the Oronoco. It possesses the usual external characters of resins, but when purified by solution in alcohol, it crystallises in small transparent prisms, and is obtained by slow crystallisation in very beautiful crystals of a fine yellow colour. According to Provostaye, they are monoclinic, exhibiting the combination $\infty P . \infty P\infty . [\infty P\infty] . oP . +P . P\infty . [P\infty]$. Angle $\infty P : [\infty P\infty] = 119°$; $\infty P : oP = 101° 7'$; $oP : [P\infty] = 143° 15'$: $\infty P : [P\infty]$ = about $98° 45'$: $\infty P\infty : P\infty = 139° 35'$; $\infty P\infty : \infty P = 150° 30'$. Ratio of axes $a : b : c = 1{\cdot}769 : 1 : 1{\cdot}347$. Angle of axes b and $c = 78° 43'$.

Maynas resin has the characters of an acid, dissolving readily, even at common temperatures, in potash, soda, and ammonia. It is insoluble in *water*, very soluble in *alcohol*, *ether*, and *oils* both fixed and volatile. Specific gravity = 1·12. It melts at about 105° to a transparent glass, and when once melted, remains liquid for a long time, not solidifying till cooled to about 90°. By *dry distillation* it yields empyreumatic oils, and leaves a carbonaceous residue. It contains, according to the mean of Lewy's analyses, 67·52 per cent. carbon and 7·30 hydrogen, whence Lewy deduces the formula $C^{14}H^{18}O^{4}$ (calc. 67·2 C, 7·2 H, and 25·6 O).

The resin dissolves in cold *acetic acid*, also in *sulphuric acid*, forming a solution of a fine red colour, from which it is precipitated by water in its original state. It is strongly acted upon by fuming *nitric acid*, yielding a non-crystallisable nitro-acid. With ordinary nitric acid it forms a volatile acid exhibiting the characters of butyric acid; the solution yields, by concentration, crystals of oxalic acid, as well as a liquid acid, the nature of which has not been determined. The resin heated with a mixture of *acid chromate of potassium* and *sulphuric acid*, gives off carbonic anhydride and formic acid. *Chlorine* and *bromine* act upon it, but without yielding definite products.

MEADOW SAFFRON. *Gratiola officinalis* (ii. 942).

MEADOW-SWEET. See Spiræa.

MECHLOIC ACID. A crystalline acid produced, together with a chlorinated resin, by the action of chlorine on meconin. It contains 48·72 per cent. carbon, 4·07 hydrogen, no chlorine; crystallises in fine prismatic needles; is soluble in potash, sparingly soluble in cold, easily in boiling water.

MECONAMIC ACID. See Meconic acid, Amides of.

MECONIC ACID. $C^7H^4O^7 = \left.\begin{matrix}C^7HO^4\\H^3\end{matrix}\right\}O^3$. *Mohnsäure. Opiumsäure.*—This acid, which is one of the constituents of opium, was discovered by Sertürner in 1805 (Gilb. Ann. lv. 72; lvii. 183; lxiv. 65), but the more exact investigation of it has been made chiefly by Robiquet (Ann. Ch. Phys. v. 282; li. 236; liii. 425), and Liebig (Ann. Ch. Pharm. vii. 37; xxvi. 113, 147).

The best method of preparing it is that of Robiquet, modified by Gregory (Ann. Ch. Pharm. xxiv. 43). Opium is exhausted with water at 38°; the extract is neutralised with coarsely pounded marble, evaporated to a syrup, and mixed with a concentrated solution of chloride of calcium, whereby the meconate of calcium is more completely separated in proportion as the liquids are more concentrated; and the precipitate is washed with water and pressed. [The mother-liquor serves for the preparation of morphine.]—1 pt. of the precipitated meconate of calcium is now suspended in a mixture of 3 pts. commercial hydrochloric acid and 20 pts. boiling water; the mixture is kept at a temperature short of 100°, and frequently shaken, till the whole is dissolved; and the acid meconate of calcium which separates on cooling is collected on linen, washed with a small quantity of water, and redissolved, after pressure, in a mixture of 3 pts. of hydrochloric acid and 20 pts. of hot water, avoiding ebullition. The liquid then yields, on cooling, crystals of meconic acid nearly free from lime, while the mother-liquor, in consequence of the excess of hydrochloric acid, contains scarcely any meconic acid. The still coloured crystals, after being washed and pressed, are dissolved in 16 pts. of hot water; the liquid is strained through linen; and the filtrate is mixed with two-thirds of the original quantity of hydrochloric acid; on cooling it yields crystals of meconic acid, free from lime, but still coloured. These crystals are suspended in cold water, neutralised with carbonate of potassium, and heated to 100° with gradual addition of water in quantity just sufficient to dissolve them; the solution, which solidifies on cooling, is well pressed (the liquid which runs off yields impure meconic acid when treated with excess of hydrochloric acid); the expressed mass, which is not yet quite white, is redissolved in the smallest possible quantity of boiling water; the solid mass obtained on cooling is again pressed; and this treatment is repeated till a pure white product is obtained. Lastly, this pure meconate of potassium is dissolved in 16 to 20 pts. of hot water; the acid meconate of potassium which separates on cooling is mixed on linen with a small quantity of cold water, pressed, and redissolved in 16 pts. of hot water; the solution is mixed with 2 or 3 pts. of hydrochloric acid; and the crystals of pure meconic acid which form on cooling are washed with cold water, and recrystallised from solution in the smallest possible quantity of boiling water. The mother-liquor expressed from the potassium-salt still yields a quantity of impure meconic acid when treated with hydro-chloric acid. Paper-filters [probably on account of the iron contained in them] cannot be used in any part of the process.

How (Ann. Ch. Pharm. lxxxiii. 350) heats the crude acid free from lime with twice its weight of water, till the whole dissolves on addition of ammonia. The solution on cooling solidifies in a crystalline mass, which may be freed by pressure from the black mother-liquor, and recrystallised two or three times from the smallest possible quantity of boiling water. From the solution in hot water, the meconic acid separates, on addition of excess of hydrochloric acid, in colourless laminæ, which are washed with cold water, and once recrystallised from boiling water.

The aqueous extract of opium might also be treated in the first instance with ammonia to precipitate the morphine, and the meconic acid afterwards precipitated by chloride of calcium; but ammonia always precipitates a certain quantity of meconic acid from the aqueous solution in the form of a calcium-salt: hence the process is attended with loss.

Meconic acid crystallises in micaceous scales or small rhombic prisms, containing 3 at. water ($C^7H^4O^7.3H^2O$), which it gives off at 100°, leaving a white, opaque, effloresced mass. It has a sour taste, and reddens litmus strongly. It dissolves readily in *water* and *alcohol*, less easily in *ether*.

Meconic acid is resolved, under various circumstances, into carbonic anhydride and comenic acid:

$$\underset{\text{Meconic acid.}}{C^7H^4O^7} = CO^2 + \underset{\text{Comenic acid.}}{C^6H^4O^5},$$

the latter frequently undergoing further transformation:—1. When dry meconic acid is *heated* to about 120°, carbonic anhydride is given off and comenic acid remains behind; at higher temperatures, the comenic acid is further resolved, partly into carbonic anhydride and pyromeconic acid, $C^5H^4O^3$, partly into water, acetic acid, empyreumatic oil, and charcoal.—2. When meconic acid is boiled with *water*, or with *hydrochloric acid*, a brown colouring matter being also produced in the former case.—3. By the action of *chlorine* or *bromine*, in presence of water, the products being carbonic anhydride and chloro- or bromo-comenic acid.—4. By boiling with excess of *ammonia*, the comenic acid being then converted into comenamic acid.—5. By heating with *iodide of ethyl*, whereby carbonic anhydride is given off, and ethyl-comenic acid produced.

Meconic acid is easily oxidised by *nitric acid*, yielding a large quantity of oxalic acid.—By boiling with strong caustic *potash* also, it yields oxalic acid, together with carbonic anhydride and a brown substance.—By *chloride* or *bromide of iodine*, it is converted into iodomecone, $C^5H^4I^6O^2$. [? impure iodoform; see p. 312.]

The aqueous solution of meconic acid is coloured deep red by *ferric chloride*, the colour not being destroyed by boiling, or by the action of dilute acids.

Meconates.—Meconic acid is tribasic, and forms three series of salts:

$$\overbrace{\begin{array}{c}\text{monometallic.}\\ C^7H^3MO^7\end{array} \qquad \begin{array}{c}\text{dimetallic.}\\ C^7H^2M^2O^7\end{array}}^{\text{Acid.}} \qquad \begin{array}{c}\text{Normal or}\\ \text{trimetallic.}\\ C^7HM^3O^7.\end{array}$$

The dimetallic meconates are neutral to vegetable colours.

Meconates of Ammonium.—The *tri-ammonic salt* is unknown. The *di-ammonic salt*, $C^7H^2(NH^4)^2O^7$, crystallises in slender needles. On passing chlorine through its solution, the *mono-ammonic salt*, $C^7H^3(NH^4)O^7.H^2O$, separates in granular crystals, sparingly soluble in cold water.

Meconates of Barium.—The *dibarytic salt* is sparingly soluble in water. Chloride of barium forms, with solutions of the alkaline meconates, white flakes soluble in acetic acid. Aqueous meconic acid forms with baryta-water a bulky yellow precipitate, probably consisting of *tribarytic meconate.*

Meconates of Calcium.—The *monocalcic salt*, $C^7H^2CaO^7.H^2O$, is precipitated by chloride of calcium from aqueous meconic acid, and from the solutions of acid, and even of neutral meconates.—The *dicalcic salt*, $C^7H^2Ca^2O^7.H^2O$, is obtained as a yellow gelatinous precipitate, on adding chloride of calcium to the solution of a meconate saturated with ammonia.

Meconates of Copper.—The monocupric salt is obtained as a yellowish-green precipitate on adding meconic acid to a solution of cupric acetate. By dry distillation it yields a large quantity of pyromeconic acid. Meconate of potassium forms an emerald-green precipitate with cupric acetate.

Meconates of Iron.—α. The *ferrous salt* is very soluble, colourless, turns red on exposure to the air, and more quickly when mixed with nitric acid.

β. *Ferric salt.* Soluble meconates added to ferric salts produce, for the most part, a deep blood-red liquid, without precipitation, even when the solutions are concentrated; but when neutral ferric sulphate is treated with meconate of ammonium, a cinnabar-coloured pulverulent precipitate is formed after a while, which is sparingly soluble in cold water and in alcohol, easily in boiling water and in dilute acids. On mixing its aqueous solution with potash, ferric oxide is precipitated, ammonia is given off, and the red colour disappears; if hydrochloric acid be then added, sufficient to saturate the alkali, the red colour reappears, but is again destroyed by excess of acid. The red precipitate, if previously dried in the air at ordinary temperatures, undergoes no alteration at 100°. Stenhouse found in five samples of it, dried at 100°, from 30·4 to 31·1 per cent. carbon, 2·1 to 2·5 hydrogen, 3·4 to 3·5 nitrogen, and 22·6 to 24·3 ferric oxide. On mixing solutions of meconic acid and ferric chloride in anhydrous ether, red-brown flocks very soluble in cold water are precipitated. Stenhouse found in three preparations (at 100°) from 25·3 to 25·9 per cent. carbon, 1·7 to 1·9 hydrogen, and 30·3 to 31·2 ferric oxide.

Meconates of Lead.—The *neutral salt*, $C^7HPb^3O^7.H^2O$, is produced by precipitating neutral acetate of lead with meconic acid, even in excess; it forms white flocks, insoluble even in boiling water.

Basic salts, containing from 68·4 to 78·4 per cent. lead-oxide, are obtained by precipitating basic acetate of lead with alkaline meconates.

Magnesium-salts.—The *dimagnesic salt* is sparingly, the monomagnesic salt easily soluble in water; the latter crystallises in shining, transparent, flattened needles, having an acid and bitter taste.

Meconates of Mercury.—Both the mercurous and mercuric salt are pale yellow flocculent precipitates, insoluble in water, soluble in nitric acid.

Meconates of Potassium.—The *acid salts* are crystallisable, the *neutral salt* uncrystallisable.

Meconates of Silver.—Aqueous meconic acid forms with nitrate of silver a white precipitate of the *di-argentic salt*, $C^7H^2Ag^2O^7$, which, by prolonged boiling with water, is converted into the *tri-argentic salt*, $C^7HAg^3O^7$. The latter is also formed, as a yellow precipitate, on mixing a solution of meconic acid, exactly saturated with ammonia (the di-ammonic salt) with nitrate of silver.

Meconates of Sodium.—The *monosodic salt* forms hard grains, but slightly soluble in water.—The *disodic salt*, obtained by digesting meconate of barium with aqueous sulphate of sodium, crystallises in slender needles, soluble in 5 pts. of water, and containing a large quantity of water of crystallisation. The *trisodic salt* is crystallisable, very soluble in water, and efflorescent.

Meconates of Tin.—The *stannous salt* is a white precipitate, very soluble in excess of the stannous solution. The *stannic salt* is also a white precipitate, sparingly soluble in acetic, easily in nitric acid.

Meconate of Yttrium.—Sparingly soluble in water; yttrium-salts, however, give no precipitate with meconic acid.

MECONIC ACID, AMIDES OF. By acting on ethyl-meconic acid and diethyl-meconic acid with ammonia, How has obtained two acids, which may be regarded as mono-ammonic meconate *minus* water, viz.:

Meconamic acid . . . . $C^7H^5NO^6 = C^7H^3(NH^4)O^7 - H^2O$
Mecono-diamidic acid . . . $C^7H^6N^2O^5 = C^7H^2(NH^4)^2O^7 - 2H^2O$

Neither of these acids has, however, been obtained in the crystalline form, and their formulæ are somewhat doubtful. To the former How assigned the somewhat improbable formula $C^{42}H^{28}N^7O^{36}$; the formula above given was proposed by Gerhardt. (*Traité*, ii. 180.)

MECONIC ETHERS. Meconic acid, being tribasic, should form three ethers containing ethyl or other alcohol-radicles. Only the two acid ethyl-meconates are, however, at present known.

ETHYL-MECONIC ACID, $C^7H^3(C^2H^5)O^7$, is obtained by passing dry hydrochloric acid gas through a solution of meconic acid in absolute alcohol, till the liquid emits fumes. It then, if left at rest, deposits the ethylated acid in needle-shaped crystals, which may be purified by recrystallisation from hot water.

The acid forms small needles very soluble in boiling water, soluble in ether and in alcohol of ordinary strength, less soluble in absolute alcohol. The crystals are anhydrous, melt at 158°, and sublime in brilliant rhombs.

Ethyl-meconic acid is dibasic, forming two series of very stable salts, viz. *neutral salts*, $C^7HM^2(C^2H^5)O^7$, and *acid salts*, $C^7H^2M(C^2H^5)O^7$. They crystallise readily. (How, Ann. Ch. Pharm. lxxxiii. 350.)

DIETHYL-MECONIC ACID, $C^7H^2(C^2H^5)^2O^7$, is contained in the mother-liquor from which ethyl-meconic acid has separated, and may be obtained by evaporating this liquid till it gives off acid vapours. The residue is a thick oil which solidifies on cooling, and may be purified by recrystallisation.

It forms flattened colourless prisms, melting at about 110°; it melts in boiling water before dissolving, and dissolves very easily in alcohol. Its aqueous solution has a strong acid reaction, decomposes carbonates, and rapidly coagulates albumin. It colours ferric salts red.

The acid is monobasic, the formula of its salts being $C^7HM(C^2H^5)^2O^7$. The *ammonium-salt* crystallises in yellow needles, and is very soluble in cold water. It is most easily prepared by passing gaseous ammonia into an alcoholic solution of the acid. The *barium-salt* is a yellow semi-gelatinous precipitate, insoluble in boiling water, but very soluble in excess of chloride of barium. The *strontium-* and *calcium-salts* resemble the barium-salt. The *magnesium-salt* is a crystalline precipitate. The *copper-salt* is green and gelatinous. The *lead-salt* is a yellowish-white precipitate. The *silver-salt* is yellow, gelatinous, insoluble in boiling water. (How, *loc. cit.*)

MECONIN. *Opianyl.* $C^{10}H^{10}O^4$.—A neutral substance existing in opium. It was first observed by Dublanc (Ann. Ch. Phys. [2] xlix. 17); afterwards prepared in the pure state, and examined by Couerbe (*ibid.* xlix. 11; l. 337; lix. 148).

It is produced from narcotine, together with teropiammone, cotarnine, opianic acid, and hemipinic acid, by the action of warm dilute nitric acid (**Anderson**, Ed. Phil. Trans. xx. 347; xxi. 204), and from opianic acid by the action of caustic alkalis, or of nascent hydrogen, evolved either by the action of sodium-amalgam on water, or of zinc on dilute sulphuric acid. (**Matthiessen** and **Foster**, Chem. Soc. J. xvi. 349.)

a. Action of alkalis:

$$\underset{\text{Opianic acid.}}{2C^{10}H^{10}O^{5}} = \underset{\text{Meconin.}}{C^{10}H^{10}O^{4}} + \underset{\text{Hemipinic acid.}}{C^{10}H^{10}O^{6}}.$$

β. Action of nascent hydrogen:

$$\underset{\text{Opianic acid.}}{C^{10}H^{10}O^{5}} + H^{2} = \underset{\text{Meconin.}}{C^{10}H^{10}O^{4}} + H^{2}O.$$

Preparation. *a. From Opium.*—1. Finely cut Smyrna opium is exhausted with cold water; the filtrate is evaporated to 8° Bm., and the morphine and narcotine are precipitated by dilute ammonia. The filtrate evaporated to a syrup, and then left for several weeks in a cool place, deposits brown crystals, which must be pressed and then dried at a gentle heat. The brown crystalline mass contains meconin, meconates, and other substances. It is exhausted with boiling alcohol of 36°, and the extracts are concentrated to one-third by distilling off the alcohol; the liquid then on cooling deposits crystals, which are purified by recrystallisation from boiling water, with addition of animal charcoal, then from hot ether. The mother-liquor from which the crystals have separated, yields an additional quantity of meconin by concentration. (**Couerbe**.)

2. The aqueous extract of opium is precipitated by chloride of calcium; the precipitated meconate of calcium is filtered; the filtrate evaporated to the crystallising point, and separated from the deposited hydrochlorate of morphine; and the dark mother-liquor is diluted with water, filtered from the flocks which separate, and treated with ammonia, which precipitates narcotine, thebaine, and a large quantity of resin. The filtrate is mixed with acetate of lead; the excess of lead is removed from the filtered liquid by dilute sulphuric acid; and the filtrate is neutralised with ammonia, and evaporated to the crystallising point at a moderate heat, whereupon narceine separates out, and then sal-ammoniac by further concentration. The mother-liquor is repeatedly digested with ½ vol. ether at 26°, and the ether is distilled off from the extracts, a brown syrup then remaining. On treating this syrup with dilute hydrochloric acid, papaverine dissolves, and meconin remains in the form of a dark grey crystalline powder, which, to free it from resin and purify it completely, must be several times crystallised from boiling water, with addition of animal charcoal. (**Anderson**.)

b. From Narcotine.—Narcotine is heated in the water-bath to 49° with 2·8 pts. of nitric acid of specific gravity 1·4, and 8 pts. water, whereupon it melts into a yellowish mass, dissolves slowly without evolution of gas, if constantly stirred, and then gradually deposits crystalline teropiammone. The liquid is filtered through asbestos; the filtrate saturated with potash-ley; the solution again filtered from precipitated cotarnine, and concentrated to a small bulk; crystallised nitre is removed, and the mother-liquor freed from carbonate of potassium by precipitation with alcohol; the alcohol is distilled off; and the cooled residue treated with hydrochloric acid, which precipitates opianic acid, hemipinic acid, and meconin. If this precipitate be dissolved in a large quantity of boiling water, meconin crystallises out on cooling (mixed with a little opianic acid, if the quantity of water added was insufficient), and may be purified by recrystallisation from water or alcohol. (**Anderson**.)

c. From Opianic acid.—1. By the action of strong caustic *potash*. This mode of preparation is described under HEMIPINIC ACID (p. 142).—2. By the action of *nascent hydrogen*. Sodium-amalgam is warmed for several hours in an aqueous solution of opianic acid; and the meconin is precipitated from the solution by hydrochloric acid. The formation of the meconin in this case is not due to the action of the caustic soda formed from the sodium-amalgam: for it takes place in a dilute solution, and at a temperature very much below that at which opianic acid is decomposed under the influence of alkali; the quantity of meconin formed is also considerably greater than that which is produced under the latter circumstances, 5 grms. opianic acid decomposed by sodium-amalgam having yielded 3·65 grms. of pure meconin, whereas, according to the first of the two equations above given, it should, when decomposed by alkalis, yield only 2·3 grms. meconin. Moreover, opianic acid is similarly converted into meconin by the action of zinc and dilute sulphuric acid. (**Matthiessen** and **Foster**.)

Properties.—Meconin crystallises in hexagonal prisms with dihedral summits. It is perfectly colourless; has no smell; and appears tasteless at first, but exhibits a very acrid taste as it dissolves in the mouth.

It melts at 90° (**Couerbe**); between 98° and 99° (M. and F.) to a colourless liquid, which retains its fluidity till cooled to 75°. At a higher temperature, it boils and distils without alteration, solidifying to a fatty mass on cooling.

A hydrate of meconin was once obtained by Anderson, in decomposing meconin with nitric acid: it resembled the anhydrous compound, but was lighter, and did not melt below 96°.

Meconin dissolves in 265·7 pts. of cold, and 18·5 pts. of boiling *water;* in *alcohol* and *ether* it is still more soluble. It is dissolved by the *fixed alkalis,* but is nearly insoluble in *ammonia.* When heated to 100° with aqueous *ammonia,* it yields a solution which may be evaporated over sulphuric acid at ordinary temperatures, but from which meconin it precipitated on addition of water (Matthiessen and Foster).—Its aqueous solution precipitates *basic acetate of lead,* but not the neutral acetate.

Meconin dissolves without alteration in *dilute sulphuric acid,* forming a colourless solution which becomes dark green when evaporated: if alcohol be then added, the liquid acquires a rose colour; but as the alcohol evaporates, the green tint returns. The green solution deposits brown flocks when mixed with water (Couerbe). With *strong sulphuric acid,* meconin forms a colourless solution which becomes purple when heated, and brown on addition of water, depositing at the same time a brown precipitate, which dissolves with rose colour in alkalis. *Nitric acid,* either dilute or concentrated, converts meconin into nitromeconin, with evolution of red vapours. With *peroxide of lead and dilute sulphuric acid,* it gives off carbonic anhydride, and forms an amorphous substance which remains dissolved.

With *chlorine,* meconin forms chloromeconin (Anderson). According to Couerbe, chlorine acts but slightly on meconin at common temperatures, but is rapidly absorbed by melting meconin, forming a red and then a dark brown mass, which melts at a higher temperature than meconin, and forms on cooling a crystalline mass containing mechloic acid (p. 859), meconin-resin, and 25·5 per cent. chlorine. Meconin is not altered by *iodine,* but when treated with *chloride of iodine,* it forms iodomeconin. With *bromine-water,* it forms bromomeconin.

Meconin dissolves without alteration in cold *hydrochloric* acid; but when heated with three times its weight of strong hydrochloric acid to 100° in a sealed tube, it is decomposed, with formation of an acid containing $C^9H^2O^4$, and separation of chloride of methyl, which quickly volatilises when the tube is opened: $C^{10}H^{10}O^4 + HCl = C^9H^8O^4 + CH^3Cl$ (Matthiesen and Foster, *unpublished experiments*). A similar decomposition is produced by *hydriodic acid.* From these results Matthiessen and Foster conclude that meconin is a methylated compound; and although the proportion of methyl contained in it has not been experimentally determined, they infer, from the analogy of other derivatives of narcotine (*q. v.*) that its rational formula is $\left.\begin{matrix}(C^8H^4O)'''' \\ (CH^3)^2\end{matrix}\right\}O^3$; that is to say, that it is the dimethylated derivative of a compound, $\left.\begin{matrix}(C^8H^4O)'''' \\ H^2\end{matrix}\right\}O^3$, not yet isolated, which may be called normal meconin.

Substitution Derivatives of Meconin.

Bromomeconin. $C^{10}H^9BrO^4$.—When bromine-water is gradually added to aqueous meconin, crystals of bromomeconin separate out, and may be purified by recrystallisation from boiling alcohol. It forms colourless needles, which melt at 167°, and behave in other respects like chloromeconin. It dissolves sparingly in *water,* more readily in *alcohol* and *ether.* (Anderson, Ann. Ch. Pharm. xcviii. 48.)

Chloromeconin. $C^{10}H^9ClO^4$. When chlorine-gas is passed into a cold saturated aqueous solution of meconin, an abundant crop of crystals quickly separates, consisting of chloromeconin, which may be purified by recrystallisation from alcohol. It is likewise produced when dry chlorine-gas is passed over melted meconin. It crystallises in colourless needles, which melt at 175°, and sublime undecomposed at higher temperatures. It dissolves sparingly in cold, somewhat more freely in boiling *water;* in *alkalis* to about the same amount as in water, and without decomposition. It is soluble in *alcohol* and in *ether.*

It dissolves in cold *sulphuric acid,* assumes a greenish-blue colour when heated therewith, and on subsequent addition of water, deposits brown flocks which dissolve with red colour in alkalis. It dissolves with red colour in *nitric acid,* and is decomposed when heated therewith. (Anderson, Ann. Ch. Pharm. xcviii. 47.)

Iodomeconin. $C^{10}H^9IO^4$.—When chloride of iodine is added to aqueous meconin, and the mixture left to itself for several days in a warm place, long crystals form in it, contaminated by free iodine. They are purified by recrystallisation from boiling alcohol.

Iodomeconin forms colourless needles, which melt at 112° to a colourless liquid. It is nearly insoluble in *water,* more soluble in *alcohol* and *ether.* It melts at a temperature above 100° to a brown liquid, which decomposes at a stronger heat with volatilisation of iodine. It dissolves in *sulphuric acid,* forming a dark-coloured liquid when heated; and is decomposed by *nitric acid,* with separation of iodine. (Anderson, *loc. cit.*)

Nitromeconin. $C^{10}H^9NO^6 = C^{10}H^9(NO^2)O^4$.—Meconin dissolves abundantly in cold concentrated nitric acid, the solution giving off red fumes when heated. On diluting with water, bulky crystals separate, which may be obtained pure by washing and recrystallisation from boiling alcohol.

Nitromeconin forms white needles and prisms, melting at 160° to a transparent liquid, which solidifies in the crystalline form on cooling. It is neutral, dissolves sparingly in cold, somewhat more freely in boiling *water;* it is insoluble in *hydrochloric acid*, but dissolves in cold strong *nitric acid*, separating in flocks when the solution is diluted. In cold *ammonia* and *potash*, it is not more soluble than in water. It is not precipitated by metallic salts. It dissolves in boiling *alcohol* and *ether*.

Heated in small quantities on platinum-foil, it volatilises almost without decomposition, leaving only a small quantity of charcoal; but, if heated in a test-tube, it decomposes suddenly, and leaves a large quantity of porous charcoal. Boiled with *ammonia* or *potash*, it forms, without decomposition, a yellow solution which does not deposit anything on cooling or on addition of acids.

MECONIUM. A substance occurring in the intestinal canal of the fœtus, and voided soon after birth: it consists, in fact, of the bile of the fœtus, which is gradually poured into the intestines, and has there undergone a certain amount of alteration. It is a pitchy substance, of a dark brown-yellow colour, and the consistence of honey. Its odour is for the most part faint, and only occasionally unpleasant; taste mawkish, and slightly sweet. It stains linen permanently yellow. In water it swells up to a bulky mass, in which the microscope shows epithelium-cells, small round bodies, probably consisting of decolorised blood-corpuscles, and a considerable number of rhombic tablets of cholesterin. According to Simon, dried meconium contains 16 pts. cholesterin, 10·4 extractive matter and bile-resin, 34 casein, 6 picromel, 4 biliverdin, 26 cells, mucus, and perhaps albumin (= 96·4). The cholesterin is extracted by ether, the extractive matter and bile-resin by alcohol. Aqueous alcohol takes up the casein together with picromel; the biliverdin may be dissolved out by alcohol acidulated with sulphuric acid.

According to John Davy, meconium contains 72·7 pts. of water, 23·6 mucus and epithelium-cells, 7·0 cholesterin and margarin, and 3·0 olein and biliary colouring matters.

When burnt, it leaves an ash consisting chiefly of ferric oxide and magnesia, with traces of calcic phosphate and sodic chloride. According to Payen, it contains common salt, alkaline carbonate and calcic phosphate. (Handw. d. Chem. v. 143.)

MEDICAGO SATIVA. *Lucern.*—The composition of the ash of this plant, as determined by Way and Ogston, is given under FODDER (ii. 680).

MEDICINIER, OIL OF. This oil, obtained by expression from the seeds of *Jatropha Curcas*, is white, scentless, has a density of 0·91 at 19°, and solidifies to a buttery mass at − 8°. It is nearly insoluble in alcohol, has a sweet taste, and alters but very little on exposure to the air. It is not easily saponified by potash, but soda easily converts it into a hard white soap, containing oleic and isocetic acids. Nitric acid converts the oil into suberic acid: pernitric oxide does not solidify it completely. When heated with ammonia, in a sealed tube, it is converted into isocetamide.

MEDJIDITE. Calcio-uranic sulphate, occurring near Adrianople. (See SULPHATES.)

MEDULLIC ACID. $C^{21}H^{42}O^2$.—A fatty acid produced, together with oleic and palmitic acids, by the saponification of beef-marrow. It forms 10 per cent. of the acid mixture thus obtained. Melting point 72·5°. (Eylerts, Arch. Pharm. [2] civ. 129.)

MEDULLIN. A name applied by Braconnot to cellulose obtained from the pith or medulla of certain plants.

MEERSCHAUM. (*Sea-foam:* from its apparent lightness and whitish colour.) A hydrated silicate of magnesium, $2Mg^2O.3SiO^2.2H^2O$, or $Mg^4Si^3O^8.2H^2O$, occurring in stratified earthy or alluvial deposits on the plains of Eskihi-sher, in Asia Minor; also in Greece, at Hrubschitz in Moravia, and in Morocco. It is compact, smooth to the touch, and of fine earthy texture. Hardness = 2 to 2·5; impressible by the nail. It is opaque and white, sometimes with a greyish, yellowish, or reddish tinge. When heated in a tube, it gives off water, blackens, and emits a burnt smell. Before the blowpipe on charcoal it burns white, and melts on the thinnest edges. It dissolves readily in borax to a transparent glass, and exhibits a lilac colour with cobalt-solution. Hydrochloric acid dissolves it, with separation of silica.

Analyses.—1. is by Lychnell (Kongl. Vetensk. Acad. Förhandlingar, 1826, p. 175); 2. By Damour (Ann. Ch. Phys. [3] vii. 316):

	SiO^2	Mg^2O	H^2O	Fe^4O^3	Al^4O^3	Ca^2O	K^2O	Sand	
1. Asia Minor	60·87	27·80	11·29	0·09		. .	. .	. .	= 100·05
2. Morocco .	55·00	28·00	10·35	1·40	1·20	1·01	0·52	1·50	= 98·98

The formula above given requires 60·9 silica, 26·1 magnesia, and 12·0 water. In these analyses, the mineral was first dried over sulphuric acid to expel hygroscopic water (of which, being porous, it contains a considerable quantity), and the combined water was then driven off by heat. The mineral is often mixed with more or less carbonate of magnesium, by the decomposition of which it appears to have been produced. (J. L. Smith, Sill. Am. J. [2] vii. 286.)

MEILER. The German name for the heaps or stacks of timber piled up for burning into charcoal. (See Carbon, i. 760.)

MEÏN. A body obtained by Reinsch from *Athamanta Meum*. The root, after exhaustion with hot water, is treated with alcohol of 70 per cent.; the alcohol is removed by distillation, and subsequent spontaneous evaporation; and the residue is digested with ether, which extracts the meïn. On evaporating the ether, the meïn remains as a thick, yellow, inodorous, combustible oil, having a burning taste, and not volatile without decomposition. (*Handwörterbuch.*)

MEGABROMITE. A variety of chlorobromide of silver from Chile, crystallised in cubes and octahedrons containing $Ag^9Br^5Cl^4$, or $4AgCl.5AgBr$. (See Silver.)

MEIONITE. A calcio-aluminic silicate from Somma, where it occurs in small dimetric crystals, in geodes, usually in limestone blocks. Ratio of the principal to the secondary axes = 1 : 0·439. Angle P : P in the terminal edges = 136° 11′; in the lateral edges = 63° 40′; these angles are nearly the same as those of scapolite (*q. v.*). Observed combination ∞P∞ . ∞P . P . ∞P3 . P∞ . 3P3 . oP. Sometimes hemihedral in the planes 3P3, the alternate ones being wanting. Cleavage parallel to ∞P∞ and ∞P, rather perfect, but often interrupted.

Hardness = 5·5 to 6. Specific gravity = 2·5 to 2·74. Lustre vitreous. Colourless to white. Transparent to translucent; often cracked within. Before the blowpipe it melts to a colourless glass; forms also a clear glass with soda. According to v. Rath, the mineral when pure, dissolves completely in moderately strong hydrochloric acid; but on heating or evaporating the solution, the silica separates in the pulverulent form. According to L. Gmelin and Kobell, it gelatinises with hydrochloric acid.

Analyses: *a.* L. Gmelin (Schw. J. xxv. 36; xxxv. 345).—*b.* Stromeyer (*Untersuchungen*, p. 378).—*c.* Wolff (*De compositione Eckebergitis, Scapolithi et Mejonitis, Dissertatio*, Berolini, 1843).—*d.* Rath (Pogg. Ann. lxxxii. 288).

	SiO^2	Al^4O^3	Fe^4O^3	Fe^2O	Ca^2O	Mg^2O	Na^2O*	K^2O.	Loss by ignition.	
a.	43·80	32·85	. .	1·07	20·64	. .	2·57	. .	. .	= 100·93
b.	40·53	32·73	. .	0·18	24·24	. .	1·81	. .	. .	= 99·49
c.	42·07	31·71	. .	. .	22·43	. .	0·45	0·31	0·31	= 97·28
d.	42·55	30·89	0·41	. .	21·41	0·83	1·25	0·93	0·19	= 98·46

* With some lithia.

These analyses lead to the formula $3(2Ca^2O.SiO^2) + 2(2Al^4O^3.3SiO^2)$, or $Ca^{12}Al^{16}Si^9O^{36}$, which, substituting $al = \frac{2}{3}$ Al, may be reduced to an orthosilicate, R^4SiO^4. (Dana, ii. 200. —*Rammelsberg's Mineralchemie*, p. 714.)

MELACONITE. Native cupric oxide, found at Copper Harbour, Kewenaw Point, Lake Superior (ii. 68).

MELAIN. This name is given by Bizio to the black substance which is deposited, together with the carbonates of calcium and magnesium, when the dried residue of the so-called ink of cuttle-fish is stirred up with water. It is contained in a peculiar bladder which the animals eject on the approach of their enemies, to render the water opaque. It may be obtained pure by boiling the above-mentioned residue with water, then with alcohol, lastly with hydrochloric acid, and washing with water containing a little carbonate of ammonium. It is insoluble in water, alcohol, and ether, but remains suspended in water for a long time. It dissolves in strong nitric and sulphuric acids, not in hydrochloric or acetic acid. Strong caustic potash dissolves it, forming a dark brown liquid, which is precipitated by sulphuric and hydrochloric acids. It is not dissolved by alkaline carbonates. These characters are very similar to those of the black pigment of the eye. (Handw. d. Chem. v. 160.)

MELALEUCA LEUCODENDRON. The tree which yields cajeput-oil (i. 710.)

MELAM. $C^6N^{11}H^9$ or $C^6N^8H^6$? (Liebig, Ann. Ch. Pharm. x. 10; liii. 240.—Knapp, *ibid.* xxi. 242.—Völckel, Pogg. Ann. lxi. 367; lxiii. 90.—Gerh. i. 464.)—A compound obtained as a residue when sulphocyanate of ammonium is heated. This salt decomposes at a temperature a little above the boiling-point of water, first giving off ammonia, then sulphide of carbon in considerable quantity, and sulphide of ammonium, and leaving a residue which Liebig calls *rude melam*. On boiling this product with moderately strong potash-ley, till the greater part is dissolved, and leaving the filtered liquid to cool, melam is deposited in the form of a white granular powder. Instead of sulphocyanate of ammonium, Liebig finds it preferable to heat a mixture of equal parts sal-ammoniac and sulphocyanate of potassium, stirring constantly till no more vapours of sulphocyanate of ammonium are evolved, and sal-ammoniac begins to sublime. The mass is then exhausted with cold water, and the residue is dried and gently ignited.

Völckel prepares melam by heating sulphocyanate of ammonium in a retort, exhausting the residue with cold water, and then with boiling water. The first decoctions deposit a bulky matter; the last, on cooling, yield melam in the form of a white powder.

Melam is a white granular powder insoluble in cold water, also in alcohol and in ether. It yields by analysis the following numbers:

	Liebig.	Völckel.
Carbon	30·49	28·37
Hydrogen	3·94	4·77
Nitrogen	65·57	66·86
	100·00	100·00

Liebig deduces from his own analysis the formula $C^6N^{11}H^9$ (calc. 30·63 carbon and 3·8 hydrogen); according to which, melam may be regarded as hexcyanopentamide, $\left.\begin{matrix}C^6N^6\\H^9\end{matrix}\right\}N^5$, or as a compound of 2 at. tricyanimide with 3 at. ammonia $= 2Cy^3N.3H^3N$. Gerhardt, on the other hand, prefers the formula $C^3N^6H^6$, which agrees better with Völckel's analysis (calc. 28·57 carbon, 4·76 hydrogen, and 66·67), and represents melam as isomeric or polymeric with melamine or cyanuro-triamide, $\left.\begin{matrix}Cy^3\\H^6\end{matrix}\right\}N^3$.

By prolonged boiling with caustic alkalis, melam is converted into melamine, which separates on evaporation or as the liquid cools. The mother-liquor contains ammeline, which may be precipitated by acids, together with ammelide; and the latter, by the continued action of the alkali, is ultimately resolved into ammonia and cyanuric acid. These changes may be represented by the following equations:

$$(1,\ a.)\quad \underset{\text{Melam.}}{C^6N^{11}H^9} + 2H^2O = \underset{\text{Ammeline.}}{2C^3N^5H^5O} + NH^3$$

$$\text{or } (1,\ b.)\quad \underset{\text{Melam.}}{C^3N^6H^6} + H^2O = \underset{\text{Ammeline.}}{C^3N^5H^5O} + NH^3$$

$$(2.)\quad \underset{\text{Ammeline.}}{C^3N^5H^5O} + H^2O = \underset{\text{Ammelide.}}{C^3N^4H^4O^2} + NH^3$$

$$(3.)\quad \underset{\text{Ammelide.}}{C^3N^4H^4O^2} + H^2O = \underset{\text{Cyanuric acid.}}{C^3N^3H^3O^3} + NH^3$$

If Gerhardt's formula of melam be admitted, the formation of melamine is a case of mere polymeric transformation: according to Liebig's formula, on the other hand, the melamine is produced by assumption of ammonia eliminated in the formation of the other products above mentioned:

$$\underset{\text{Melam.}}{C^6N^{11}H^9} + NH^3 = \underset{\text{Melamine.}}{2C^3H^6H^6}$$

Melam is resolved by *heat* into ammonia and mellone or hydromellone (perhaps thus: $C^6N^{11}H^9 = 2NH^3 + C^6N^9H^3$). When boiled with dilute hydrochloric or sulphuric acid, or when treated with nitric acid, it yields ammeline; with concentrated sulphuric acid, the same, together with ammelide. By boiling with strong nitric acid, it is converted into cyanuric acid; and by fusion with hydrate of potassium, it forms cyanate of potassium.

According to Völckel, melam absorbs hydrochloric acid gas, forming the compound $C^3N^6H^6.HCl$.

MELAMINE. $C^3N^6H^6$.—Syn. with CYANURAMIDE (ii. 287).

MELAMPYRIN or **MELAMPYRITE.** Syn. with DULCITE (ii. 348).

MELANASPHALT. A kind of bituminous coal found in Nova Scotia.

MELANOCHLOR. A blackish-green phosphate of iron from Rabenstein, containing in 100 pts. 38·9 per cent. ferric and 8·87 ferrous oxide, besides manganous oxide and 9 to 10 per cent. water. (Fuchs, J. pr. Chem. xvii. 171.)

MELANGLANCE. Native sulphide of silver. (See SILVER.)

MELANHYDRITE. A mineral found in the greywacke formed from decomposed basalt in the Schmelzerthal, near Honnef on the Rhine. It is deposited in the rock in amorphous nodular particles, of conchoïdal fracture; opaque, with velvet-black, sometimes brownish-black colour, and blackish-brown streak; small lumps adhere to the tongue; it does not fall to pieces in water. Specific gravity = 1·820. Rammelsberg found in it:

SiO^2	Al^4O^3	Fe^4O^3	Fe^2O	Mn^2O	Mg^2O	Ca^2O	H^2O	
41·63	18·72	2·36	7·83	2·51	5·23	1·67	20·71	= 100·66;

whence the formula $3M^2O.2M^4O^3.6SiO^2.12H^2O$, showing that the mineral is related in composition to palagonite. (Krantz, Jahresb. 1859, p. 795.)

MELANIC ACID. $C^{10}H^8O^5$. (Piria, Ann. Ch. Phys. [2] lxix. 281.)—A black substance produced, together with acetate of potassium, by the oxidation of salicylide of potassium. This compound, when exposed in a slightly moist state to the air, becomes covered with spots, which are green at first, but ultimately become quite black. This change does not take place in an atmosphere free from oxygen; but if the experiment be made under a bell-jar filled with oxygen, the whole of that gas is gradually absorbed, and no other gas is evolved.

The reaction may be represented by the following equation:

$$\underset{\text{Salicylide of potassium.}}{2C^7H^5KO^2} + O^2 + 2H^2O = \underset{\text{Melanic acid.}}{C^{10}H^8O^5} + \underset{\text{Acetate of potassium.}}{2C^2H^3KO^2}.$$

When the transformation is complete, a carbonaceous mass remains, from which water extracts acetate of potassium, while melanic acid remains undissolved in the form of a powder resembling lamp-black. It is tasteless, insoluble in water, very soluble in alcohol, ether, and alkaline liquids, and precipitated from the latter by acids. It decomposes alkaline carbonates.

Melanic acid gives by analysis 56·26 and 56·56 per cent. carbon, and 4·01 hydrogen: the formula $C^{10}H^8O^5$ requires 59·69 carbon, 3·84 hydrogen, and 38·47 oxygen.

A black substance having nearly the same composition is obtained by the action of alkalis on quinone.

Melanate of ammonium is obtained by digesting melanic acid with ammonia. *Melanate of silver* is a black precipitate containing 27·27 per cent. carbon, 1·95 hydrogen, and 48·00 silver.

MELANILINE. See ANILINE, DERIVATIVES OF, under PHENYLAMINES.

MELANIN. The black pigment of the eye (ii. 615).

MELANITE. A black calcio-ferric garnet (ii. 772), found chiefly near Albano and Frascati, in the neighbourhood of Rome.

MELANOCARBIMIDE. $C^{14}H^{11}N^3O$.—A substance probably formed by the decomposition of melanoximide (*q. v.*).

MELANOCHIN. A doubtful product, formed, according to Brandes and Leber (Arch. Pharm. xv. 259), together with several others, by the action of ammonia and chlorine upon quinine (*q.v.*).

MELANOCHROITE. A basic chromate of lead, $Pb^2O.4PbCrO^4$, found at Beresof in the Ural (i. 934).

MELANOGALLIC ACID. Syn. with METAGALLIC ACID.

MELANOLITE. A mineral having the aspect of chlorite, from Milk Row Quarry, near Charlestown, Massachusetts. It is black and opaque, with a striated surface, and somewhat columnar structure. Streak dark olive-green. Hardness = 2. Specific gravity = 2·69. According to H. Wurtz, it contains 30·86 per cent. silica, 3·92 alumina, 20·25 ferric oxide, 21·97 ferrous oxide, 1·62 soda, and 8·94 water, with 12·77 carbonate of calcium = 100·33. This composition, deducting the calcic carbonate, may be represented by the formula $2(M^2O.SiO^2).M^4O^3.SiO^2 + 3H^2O$; but the mineral is perhaps not of constant composition (Dana, ii. 288). Rammelsberg (*Mineralchemie*, p. 539) observes that it is near Hisingerite.

MELANOXIMIDE. $C^{15}H^{14}N^6O^2$.—A product of the decomposition of cyanomelaniline. (See MELANILINE, under PHENYLAMINES.)

MELANTERITE. Native ferrous sulphate. (See SULPHATES.)

MELANURENIC ACID. See CYANURAMIC ACIDS (ii. 287).

MELAPHYRE. The name given by Von Buch to a porphyritic rock, consisting of a black or blackish-grey matrix of labrador and augite, in which are imbedded crystals of the same minerals, and sometimes, as accessory constituents, uniaxial mica, hornblende, and iron pyrites. It sometimes has the structure of almond-stone, with spherical and almond-shaped nodules of calcspar, zeolites, &c. Melaphyre occurs in the Alps, especially in the Fassa valley, and near Klausen, in the Tyrol; also in the Lower Rhine, on the Fichtelgebirge; at Friedrischrode, in the Thüringer Wald; and at Holmestrand, in South Norway.

MELASSIC ACID. A black acid, produced, together with glucic acid (ii. 848), by heating glucose with caustic alkalis. When glucose is melted at 100°, and a hot saturated solution of baryta is added, a very violent action takes place, giving rise in the first instance to the formation of glucic acid; but if the mixture be exposed for some time to a high temperature, it becomes continually darker in colour, in consequence of the formation of melassic acid. On dissolving the residue in water and precipitating by hydrochloric acid, melassic acid is deposited in black flocks insoluble in water, but soluble in alcohol. It contains, according to Peligot's analysis, 61·9 to 61·0 per cent. carbon, and 5·3 to 5·4 hydrogen. The formula $C^{12}H^{10}O^5$, requiring 61·9 carbon, 4·3 hydrogen, and 33·8 oxygen, agrees with these results so far as the carbon is concerned; but the amount of hydrogen found by experiment is too large for it.

MELENE. $C^{60}H^{60}$. *Paraffin of Wax.* (Ettling, Ann. Ch. Pharm. ii. 252.—Lewy, Ann. Ch. Phys. [3] v. 395.—Brodie, Ann. Ch. Pharm. lxxi. 156.)—A substance homologous with ethylene, &c., produced by the dry distillation of hydrate of myricyl and of myricin. It may be prepared by subjecting bees'-wax to dry distillation, treating the product with potash, to saponify the fatty acid formed at the same time; decanting the soap from the mixture of melene and oily hydrocarbons; and distilling this mixture, which then gives off, first, the oily hydrocarbons, and, lastly, the melene, when the heat is considerably increased. The product is purified by pressure and recrystallisation from boiling ether. It is generally necessary, however, before crystallising it, to rectify it over caustic potash, in order to remove a small quantity of an oxygenated substance with which it is still contaminated.

Melene crystallises in perfectly white nacreous scales, inodorous and tasteless, of specific gravity 0·89. It melts at 62° (Brodie), at 33·5° (Ettling), at 47·8° (Lewy), and solidifies in a waxy mass on cooling. Boils between 370° and 380°. Vapour-density, by three experiments, between 10·0 and 11·8: the determinations were, however, rendered inaccurate by partial decomposition. It is insoluble in water and in cold alcohol, but dissolves in boiling alcohol, and easily in ether, and in oils both fixed and volatile.

Melene is not attacked by *potash* or *soda*, even at the boiling heat. *Sulphuric acid* does not attack it at ordinary temperatures; but on applying heat, part of the melene is carbonised, while the rest sublimes. It is but slightly attacked by boiling *nitric acid. Chlorine* attacks it, producing, under certain circumstances, a body containing a considerable amount of chlorine.

Related to melene are the several mineral tallows, distinguished as *fichtelite, hartite, hatchetin, ixolyte, kœnlite, ozokerite, scheererite, &c.*

MELENE, SULPHIDE OF. This name was applied by Völckel to a sulphuretted residue obtained, together with others (called respectively *sulphide of alphene, xanthene, xuthene,* &c.), by the action of heat on persulphocyanic acid. These residues are yellow or brown powders varying in composition according to the degree of heat applied, and are probably mere mixtures. (See Gmelin's *Handbook*, ix. 394.)

MELETIN. This name is given by W. Stein (J. pr. Chem. lxxxv. 351) to the substance produced, together with glucose, by the action of acids on rutin. This substance, according to most authorities, is identical with quercetin, $C^{23}H^{16}O^{10}$; but, according to Stein, it differs from quercetin, and has the composition $C^{23}H^{14}O^9$. It forms yellow crystals which act on polarised light, and reduce potassio-cupric tartrate. (See QUERCETIN and RUTIN.)

MELIN. See RUTIN.

MELINOPHANE. A mineral from the zircon-syenite of Norway, nearly related to leucophane. The crystals are optically uniaxial, but it has not been determined whether they are dimetric or hexagonal. It also occurs massive, with a scaly and sometimes foliated structure; cleavable in one direction. Hardness = 5. Specific gravity = 3·0. Lustre vitreous. Colour, sulphur-, citron-, or honey-yellow. Not phosphorescent. Brittle. It contains, according to an approximate analysis by Richter, 44·8 per cent. silica, 2·2 glucina, 12·4 alumina, 1·4 manganic oxide, 1·1 ferric oxide, 31·5 lime, 0·2 magnesia, 2·6 soda, 2·3 fluorine, and 0·3 nickel-oxide, zirconia, ceric oxide, and yttria.

MELEZITOSE. $C^{12}H^{22}O^{11}$.—A kind of sugar discovered in the manna of Briançon (p. 822) by Bonastre, and further investigated by Berthelot (Ann. Ch. Phys. [3] lv. 282). The extract of this substance prepared with boiling alcohol deposits melizitose after being evaporated to a syrup, and left to stand for several weeks; the product may be purified by recrystallisation from boiling alcohol.

Melezitose forms very small, short, hard, shining crystals, resembling those of cane-sugar under the microscope, white and mealy when seen in mass; it effloresces readily when exposed to the air, and gives off 4 per cent. of water when heated; melts below 140° without further alteration, and solidifies to a glass on cooling. It is about as sweet as glucose. Dextro-rotatory; for the transition-tint, $[\alpha] = 94{\cdot}1°$ for $C^{12}H^{11}O^{11}$.

It dissolves readily in *water*, and is precipitated by an *ammoniacal solution of neutral acetate of lead*. It is nearly insoluble in cold, slightly soluble in boiling *alcohol*, quite insoluble in *ether*. Absolute alcohol precipitates it from the aqueous solution.

Melezitose decomposes at about 200°. It is carbonised by cold strong *sulphuric acid*, quickly turns brown with boiling *hydrochloric acid*, and forms oxalic acid with *nitric acid*. By an hour's boiling with *dilute sulphuric acid*, it is converted into glucose. In contact with *yeast*, it passes slowly, or sometimes not at all, into vinous fermentation. It is not altered at 100° by aqueous *alkalis*, and scarcely by *potassio-cupric tartrate*.

MELILOT-CAMPHOR. See COUMARIN (ii. 93).

MELINUM. Syn. with CADMIUM.

MELISSA, OIL OF. A volatile oil contained in balm (*Melissa officinalis*), most abundantly at the flowering time, and obtained from it by distillation with water. It is colourless or pale-yellow; of specific gravity 0·85 to 0·82; has a peculiar odour; reddens litmus slightly. According to Bizio (Brugn. Giorn. xix. 360), it contains a camphor in solution. It dissolves in 5 to 6 pts. of *alcohol* of specific gravity 0·856. It dissolves *iodine*, with great rise of temperature and evolution of vapour, and becomes viscid. With *nitric acid*, it turns brown, gives off a large quantity of gas when heated, and becomes resinous. (Zeller, *Stud. über äther. Oele.*, Landau, 1850.)

MELISSIC ACID. $C^{30}H^{60}O^{2} = \left.\begin{matrix}C^{30}H^{59}O\\ H\end{matrix}\right\}O$.—(Brodie, Ann. Ch. Pharm. lxxi. 156.)—A fatty acid obtained by treating hydrate of myricyl (melissic alcohol) with potash-lime. It bears considerable resemblance to cerotic acid (i. 836), but melts at a higher temperature, viz. at 88° or 89°. According to Brodie's analysis, it contains 79·19 to 79·97 per cent. carbon, and 13·00 to 13·63 hydrogen (calc. 79 64 carbon, 13·27 hydrogen, and 7·09 oxygen). The silver salt, $C^{30}H^{59}AgO^{2}$, is a white precipitate containing 19·30 to 19·74 per cent. silver (calc. 19·30).

MELISSIN. Syn. with MELISSIC ALCOHOL, or HYDRATE OF MYRICYL. (See MYRICYL.

MELITOSE. $C^{12}H^{22}O^{11}$.—A kind of sugar obtained from the manna which falls in opaque drops from various species of *Eucalyptus* growing in Tasmania. It was first recognised as a distinct substance by Johnston (Mem. Chem. Soc. i. 159), more fully examined by Berthelot (Ann. Ch. Phys. [3] xlvi. 66.—*Chimie organique*, Par. 1860, ii. 260). It is extracted from the manna by water, and crystallises in extremely thin interlaced needles, having a slightly saccharine taste.

The crystals of melitose are hydrated, containing $C^{12}H^{22}O^{11}.3H^{2}O$. They give off 2 at. water at 100°, and become anhydrous at 130°. They dissolve in 9 pts. of cold *water*, very easily in boiling water, and dissolve also in boiling *alcohol* more freely than mannite. The alcoholic solution yields small but well-developed crystals. The aqueous solution turns the plane of polarisation to the right: for the transition-tint $[\alpha] = +102°$.

Melitose heated with *dilute sulphuric acid* is resolved into a fermentable sugar (probably dextro-glucose), and non-fermentable eucalyn (ii. 601):

$$\begin{array}{ccccccc} C^{12}H^{22}O^{11} & + & H^{2}O & = & C^{6}H^{12}O^{6} & + & C^{6}H^{12}O^{6} \\ \textbf{Melitose.} & & & & \textbf{Glucose.} & & \textbf{Eucalyn.} \end{array}$$

Melitose ferments in contact with *yeast*, but it is resolved, in the first instance, into glucose and eucalyn: consequently, since the latter is unfermentable, the quantities of alcohol and carbonic anhydride obtained from it are only half of those which would be yielded by an equal quantity of glucose. It does not reduce an alkaline *cupric* solution, and is not altered by boiling with dilute *alkalis* or with *baryta-water*. It is oxidised by *nitric acid*, yielding a certain quantity of mucic acid, together with a large quantity of oxalic acid.

MELLAMIC ACID. Syn. with EUCHROIC ACID (ii. 601).

MELLAN. Syn. with MELLONE.

MELLIC ACID. Syn. with MELLITIC ACID.

MELLILITE.—*Humboldtilite. Somervillite. Zurlite.*—A silicate occurring on

Vesuvius and at Capo di Bove, near Rome, in dimetric crystals, in which the principal is to the secondary axes as 0·6432 : 1. Observed combination oP . ∞P . ∞P∞ . P∞ . ∞P2. Angle oP : P∞ = 147° 15′; P∞ : P∞ (over ∞P∞) = 65° 30′; P∞ : P∞ (over terminal edge) = 134° 48′. Cleavage basal, distinct. Hardness = 5. Specific gravity = 2·9 to 3·104. The crystals are brown or yellow, with vitreous lustre, generally translucent, sometimes opaque. Fracture conchoïdal to uneven. Before the blowpipe it fuses with difficulty to a yellowish or black glass. Gives, with fluxes, the reactions of iron and silica. Gelatinises with acids.

Analyses.—*a. Humboldtilite*, from Somma, by Kobell (Schw. J. lxiv. 293).—*b.* The same by Damour (Ann. Ch. Phys. [3] x. 59).—*c, d. Mellilite*, from Cape di Bove, by Damour (*loc. cit.*).

	SiO^2	Al^4O^3	Fe^4O^3	Fe^2O	Ca^2O	Mg^2O	Na^2O	K^2O		
a.	43·96	11·20	. .	2·32	31·96	6·10	4·28	0·38	=	100·20
b.	40·60	10·88	4·43	. .	31·81	4·54	4·43	0·36	=	98·05
c.	39·27	6·42	10·17	. .	32·47	6·44	1·95	1·46	=	98·18
d.	38·34	8·61	10·02	. .	32·05	6·71	2·12	1·51	=	99·36

These analyses may be approximately represented by the formula $6(2Ca^2O.SiO^2) + 2(Al^4O^6 ; Fe^4O^3).3SiO^2$, which is that of an orthosilicate, the calcium being partly replaced by magnesium, sodium, and potassium.

Massive Gehlenite, which contains, according to Kobell (Kastn. Arch., iv. 313), 39·80 per cent silica, 12·80 alumina, 2·57 ferric oxide, 37·64 lime, 4·64 magnesia, 0·30 potash, and 2·00 water, may be included in the same general formula.

Somervillite, occurring on Vesuvius in dull yellow crystals, has the angles of this species. (Descloizeaux.)

MELLIMIDE. Syn. with MELLITIMIDE.

MELLITAMIC ACID. See MELLITIC ACID, AMIDES OF.

MELLITE, or *Honeystone.*—Native mellitate of aluminium (p. 871).

MELLITIMIDE. See MELLITIC ACID, AMIDES OF.

MELLITIC ACID. $C^4H^2O^4 = \left.\begin{matrix}(C^4O^2)''\\H^2\end{matrix}\right\}O^2$. *Mellic acid. Mellithsäure. Honigsteinsäure.* (Gm. x. 1.—Gerh. iii. 822.)—This acid, which was discovered by Klaproth in 1799, occurs as mellitate of aluminium, in honeystone or mellite, which is the only known source of it. There is a statement by Hünefeld (Schw. J., xlix. 215), that it may be produced by treating amber with hot hydrochloric acid; but it has not been confirmed.

To prepare it, powdered honeystone is treated with solution of carbonate of ammonium, the liquid is boiled till the excess of the ammonium-salt is expelled; caustic ammonia is added to precipitate any alumina that may have been dissolved; the liquid is filtered and evaporated till neutral mellitate of ammonium crystallises out; and this salt is purified by recrystallisation from water, a small quantity of ammonia being each time added, to reconvert the acid salt produced by evaporation of the ammonia into the crystallisable neutral salt. The purified ammoniacal salt is finally dissolved in water; the solution precipitated with acetate of lead or nitrate of silver; the washed precipitate decomposed by sulphydric acid if it contains lead, or by hydrochloric acid if it contains silver; and the liquid filtered and evaporated, whereby the excess of hydrochloric acid is expelled. (Wöhler, Ann. Ch. Pharm. xxxvii. 263.)

The lead-precipitate contains ammonia, which is transferred to the separated acid. Either, therefore, the acid must be re-precipitated with acetate of lead; the precipitate, which still contains a small quantity of ammonia, washed and again decomposed with sulphydric acid; and the acid thus liberated precipitated a third time with hydrochloric acid, in order to obtain a precipitate free from ammonia, and thence to separate the pure acid by sulphydric acid;—or the ammonium-salt must be boiled with excess of baryta-water; the resulting barium-salt decomposed by digestion with dilute sulphuric acid; the liquid filtered and evaporated till it crystallises; and the crystals freed from adhering sulphuric acid by recrystallisation. (Erdmann and Marchand.)

To prepare colourless mellitic acid from the brown acid mother-liquor obtained in the preparation of mellitate of ammonium, the colouring matter may be precipitated by chloride of barium; the mellitate of barium thrown down from the filtrate by ammonia, or by boiling with acetate of ammonium, and converted into mellitate of ammonium by digestion with carbonate of ammonium;—or the brown mother-liquor may be precipitated by a strong solution of sulphate of copper, and the crystallised mellitate of copper decomposed by sulphydrate of ammonium.—In precipitating the purified ammonium-salt by nitrate of silver, it is necessary to drop the former into an excess of the latter; otherwise the precipitate will retain ammonia. (Schwarz.)

Mellitic acid, as obtained by evaporation, is a white powder, exhibiting scarcely any appearance of crystalline structure; as crystallised from solution in cold alcohol by spontaneous evaporation, it forms delicate, silky needles, united in stellate groups. It dissolves readily in *water* as in *alcohol*. It is fusible by heat, tastes strongly acid, and is permanent in the air. (Wöhler.)

The crystallised acid does not give off water at 100°, but at a higher temperature it sublimes partly unaltered: the greater portion is, however, decomposed with separation of charcoal. According to Erdmann (J. pr. Chem. lii. 432), the sublimate obtained by heating mellitic acid consists of pyromellitic acid, C^5HO^4, which melts in the neck of the retort, and solidifies in a radiated crystalline mass. Mellitic acid, when heated in the *air*, burns with a bright sooty flame, leaving a large quantity of charcoal, which afterwards burns completely away. It is not decomposed by boiling *nitric* or *sulphuric acid*, but the latter dissolves it.

Mellitates.—Mellitic acid is dibasic, yielding neutral salts, $C^4M^2O^4$, and acid salts, C^4HMO^4. The mellitates are decomposed by heat, yielding a large quantity of charcoal, and a small quantity of products containing hydrogen. When slowly distilled with sulphuric acid, they yield pyromellitic acid, together with carbonic oxide, carbonic anhydride, and, towards the end, sulphurous anhydride.

The mellitates of ammonium, potassium, and sodium dissolve readily in water. The zinc- and manganese-salts dissolve more readily in cold than in hot water. The rest are insoluble or sparingly soluble in water.

Mellitate of Aluminium, $2Al^4O^6.3C^8O^6.36H^2O = C^{12}(Al^4)^{vi}O^{12}.18H^2O$, or $C^4al^2O^4.6H^2O$.—This compound occurs native as *mellite* or *honeystone*, in lignite, at Asten in Thuringia, near Bilin in Bohemia, and near Walchau in Moravia, both crystallised and in massive nodules. The crystals are dimetric, exhibiting the combination P . ∞P . oP . P, &c., the P-faces usually predominating. Length of principal axis = 0·7453. Angle P : P (terminal) = 118° 4′; P : ∞P (lateral) = 93° 22′; P : ∞ P = 120° 58′. Cleavage imperfect, parallel to P. Hardness = 2 to 2·5. Specific gravity 1·55 to 1·642. Lustre resinous, inclining to vitreous. Colour honey-yellow, sometimes reddish or brownish; rarely white. Streak white. Transparent to translucent, and with strong double refraction. Fracture conchoïdal. Sectile.

The crystals contain 14·5 per cent. alumina and 44·1 per cent. water of crystallisation, which is driven off at a temperature near the boiling-point of sulphuric acid. Caustic alkalis decompose them, setting the alumina free. They are dissolved by nitric acid, and separate from the solution without change of form or constitution.

Native honeystone contains a small quantity of a yellow resin, to which it owes its colour, and probably also its odour.

Mellitate of potassium, added to a solution of alum, forms a crystalline precipitate containing 9·5 per cent. alumina and 48·0 per cent. water; probably an acid salt. (Wöhler.)

Mellitates of Ammonium—The *neutral salt*, $C^4(NH^4)^2O^4.3H^2O$, forms large shining transparent crystals, having a slight acid reaction. They exhibit two forms, probably with different amounts of water; both belonging to the trimetric system, but differing considerably in the angles.

The crystals α are derived from an octahedron whose axes are to one another as √ 8·290 : √ 7·881 : 1. Observed combination oP. ∞ P. ∞ $\bar{P}$∞ . $\breve{P}$∞ . $\bar{P}$ ∞. Angle oP : $\bar{P}$∞ = 151° 8′; oP : $\breve{P}$ ∞ = 160° 24′; ∞P : ∞P = 144° 16′; ∞ P : ∞$\breve{P}$∞ = 122° 5′. The faces ∞$\breve{P}$∞ are longitudinally striated. No cleavage parallel to oP.

The crystals β are derived from an octahedron whose axes are to one another as √ 2·675 : √ 7·923 : 1. Observed combination oP . P . ∞P . ∞$\breve{P}$∞. Angle oP : P = 144° 44′; P : P = 146° 17′; P : ∞P = 125° 16′; ∞P : ∞P = 119° 41′; ∞P : ∞$\breve{P}$∞ = 120° 9½′. Cleavage parallel to oP.

The crystals give off 24·1 per cent. water (1 at.) at 100°, and at 150° decomposition takes place, with evolution of large quantities of ammonia and water, and formation of paramide and euchroate of ammonium.

$$\underset{\text{Mellitate of ammonium.}}{C^4(NH^4)^2O^4} = \underset{\text{Paramide.}}{C^4H\overset{\cdot\cdot}{N}O^2} + NH^3 + 2H^2O.$$

$$\underset{\text{Mellitate of ammonium.}}{3C^4(NH^4)^2O^4} = \underset{\text{Euchroate of ammonium.}}{C^{12}H^2(NH^4)^2N^2O^6} + 2NH^3 + 4H^2O.$$

The *acid salt*, $2C^4H(NH^4)O^4.C^4H^2O^4.4H^2O$, is obtained by decomposing ammonio-cupric mellitate with sulphydric acid. It crystallises in trimetric prisms, having their lateral edges truncated. Observed combination oP . ∞P . ∞$\breve{P}$∞ . ∞$\bar{P}$∞. Angle ∞P : ∞P = 122°.

Mellitate of Barium, $C^4Ba^2O^4.H^2O$, obtained by double decomposition, is a white gelatinous precipitate, which after a while crystallises in scales, or, if the solutions from which it was formed were very dilute, in needles. Mellitic acid added to chloride of barium forms, after a few seconds, a precipitate composed of needle-shaped crystals.

Mellitate of Calcium is obtained on mixing mellitate of ammonium with chloride of calcium, as an amorphous precipitate, which soon becomes crystalline. Mellitic acid added to lime-water throws down white flocks soluble in hydrochloric acid.

Mellitate of Cobalt, $C^4Co^2O^4.6H^2O$, crystallises from solution in boiling water in microscopic prisms.

Mellitates of Copper.—The *neutral salt*, $C^4Cu^2O^4.4H^2O$, is produced as an amorphous precipitate, becoming crystalline after a while, on mixing boiling solutions of mellitic acid and cupric acetate. On mixing cold solutions of mellitic acid and cupric acetate, there is deposited an *acid salt*, $C^4Cu^2O^4.C^4CuHO^4.8H^2O$, which also becomes crystalline. On adding a solution of cupric sulphate to a salt of mellitate of ammonium, a crystalline precipitate is formed consisting of *ammonio-cupric mellitate*, $C^4Cu^2O^4.C^4Cu(NH^4)O^4.4H^2O$, or $C^8Cu^3(NH^4)O^8.4H^2O$.

Mellitates of Iron.—The *ferric salt* is a cream-coloured precipitate, soluble in hydrochloric acid.—*Ferrous salts*. Mellitate of ammonium forms with ferrous sulphate a greenish-white precipitate, which redissolves when the liquid is warmed; but on raising the temperature to the boiling point, a basic salt, $Fe^2O.C^4Fe^2O^4.3H^2O$, is precipitated in microscopic cubo-octahedrons of a lemon-yellow colour; very sparingly soluble in water, easily soluble in hydrochloric acid; assuming an olive-green colour when dry; and giving off all their water of crystallisation at 190°.

Mellitate of Lead. $C^4Pb^2O^6$ (at 180°).—Bulky white precipitate, soluble in nitric acid; obtained by adding the acid or the ammonium-salt to acetate or nitrate of lead.

Mellitate of Magnesium. $C^4Mg^2O^4.6H^2O$.—Precipitated on adding carbonate of magnesium to a hot aqueous solution of mellitic acid, as an oil which solidifies to a crystalline mass on cooling.

Mellitate of Manganese. $C^4Mn^2O^4.6H^2O$.—Obtained in like manner. White powder, composed of microscopic needles; more soluble in cold than in boiling water, which dissolves only $\frac{1}{800}$ of it.

Mellitates of Mercury.—The *mercuric salt*, $C^4Hg^2O^4.2H^2O$, or $C^4Hhg''O^4.2H^2O$ (at 100°), is obtained as a white granular mass by triturating mercuric oxide with mellitic acid and a small quantity of water, or by precipitating an alkaline mellitate with mercuric nitrate.

The *mercurous salt*, $C^4Hhg^2O^4.2H^2O$ (at 100°), is also obtained by precipitation, as a white granular precipitate, very soluble in nitric acid, becoming anhydrous at 190°.

Mellitate of Nickel, $C^4Ni^2O^4.8H^2O$.—When a hot solution of mellitic acid is saturated with carbonate of nickel, a green semi-fluid mass separates, which hardens and becomes vitreous in contact with the air. This salt is very slightly soluble in water, very freely in dilute hydrochloric and nitric acids. It gives off half its water (4 at.) at 100°, and the rest at 300°.

Mellitates of Palladium.—Mellitic acid is perfectly neutralised by oxide of palladium; but the liquid does not yield any crystals, even when concentrated to a syrup; but on evaporation to dryness, it leaves a brown amorphous residue of *palladious mellitate*. This salt dissolves in ammonia, forming a colourless liquid, which, on evaporation, deposits colourless rhombic crystals, often macled in twos and threes, and containing $4NH^3.C^4Pd^2O^4.2H^2O$. The whole of the water is given off at 100°, together with a small quantity of ammonia. (Karmrodt, Ann. Ch. Pharm. lxxxi. 164.)

Mellitate of Palladium and Potassium crystallises from the mixture of the two salts evaporated to a syrup, in nodular groups of indistinct prisms. *Mellitate of palladium and sodium* crystallises in macled triangular pyramids containing 34 per cent. palladium. (Karmrodt.)

Mellitates of Potassium.—The *neutral salt*, $C^4K^2O^4.3H^2O$, forms efflorescent trimetric crystals, isomorphous with the neutral ammonium-salt *a*. Observed combination $oP\ .\ \infty P\ .\ \infty\breve{P}\infty\ .\ \breve{P}\infty\ .\ \breve{P}\infty$. Angle $\infty P : \infty P = 114°$; $\infty P : \breve{P}\infty = 151°$; $oP : \breve{P}\infty = 160°$; $\infty P : \infty\breve{P}\infty = 123°$ nearly.

Acid salt, $C^4HKO^4.2H^2O$.—A hot solution of 1 at. of the neutral salt and 1 at. mellitic acid yields this salt on cooling in large transparent right rhomboïdal prisms, often truncated on the lateral and terminal edges. It is more soluble in water than the neutral salt.

A compound of *acid mellitate and nitrate of potassium*, $4C^4HKO^4.NKO^3.3H^2O$, is formed by treating the preceding salt with nitric acid, or by mixing a concentrated solution of neutral potassic mellitate with nitric acid, as long as any precipitate is formed, and heating the liquid till the precipitate disappears. The double salt then crystallises in six-sided trimetric prisms with dihedral summits, exhibiting the combination $\infty P \,.\, \infty \bar{P} \infty \,.\, \breve{P} \infty$. It has an acid taste, and is but slightly soluble in water.

Another acid mellitate of potassium (perhaps $C^4HKO^4.C^4K^2O^4.6H^2O$) is mentioned by **Erdmann** and **Marchand** (J. pr. Chem. xliii. 129) as having been obtained in the form of a crystalline powder on adding mellitic acid to a concentrated solution of the neutral salt. This powder redissolved in water yielded large nacreous crystals containing 20·63 per cent. carbon, 2·74 hydrogen, and 30·49 potash.

Mellitates of Silver.—The *argentic salt*, $C^4Ag^2O^4$, is obtained on adding mellitic acid or mellitate of ammonium to nitrate or acetate of silver, as a white crystalline, shining, scaly powder, which the microscope shows to consist of transparent, colourless, square plates, usually having their angles truncated. When heated, it deflagrates slightly, but without exhibiting any electric excitement, as the oxalate does under similar circumstances. Heated to 100° in a stream of hydrogen, it blackens and gives off water, and the residue dissolves in water, forming a dark-brown, strongly acid liquid, which gradually deposits a mirror of metallic silver, leaving a solution of argentic mellitate in mellitic acid. The brown or black residue obtained by heating the argentic salt evidently contains *argentous mellitate*. When argentic mellitate previously heated to 280° is heated with iodine, iodide of silver is formed, together with a white crystalline sublimate, strongly acid, and very soluble in water.

Potassio-argentic Mellitate, C^4KAgO^4, is deposited from a mixture of the component salts containing nitric acid, in small, transparent rhombic prisms, in which the angle $\infty P \,.\, P = 121° \, 30'$; $\infty P : \infty \bar{P} \infty = 119° \, 11'$.

These crystals, when heated, first give off water and become opaque, then swell up with a kind of explosion, and leave a residue of silver and potassic carbonate.

Mellitate of Sodium, $C^4Na^2O^4$, crystallises with two different proportions of water. A hot concentrated solution deposits needles containing 32·81 per cent. (4 at.) water, the whole of which is given off at 180°. A solution saturated in the cold yields, by spontaneous evaporation, large striated triclinic crystals containing 38·88 per cent. (6 at.) water, which they give off at 160°. (**Erdmann** and **Marchand**.)

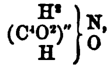
Mellitate of Strontium.—White precipitate, soluble in hydrochloric acid, obtained by adding mellitic acid to strontia-water.

MELLITIC ACID, AMIDES OF. (**Wöhler**, Ann. Ch. Pharm. xxxvii. 268.—R. **Schwarz**, *ibid.* lxvi. 52.)—Two of these compounds are obtained by the dehydration of mellitate of ammonium, viz., **mellitimide** or **paramide**, which has the composition of acid mellitate of ammonium minus 2 at. water:

$$\underset{\text{Acid mellitate of ammonium.}}{C^4H(NH^4)O^4} \quad - \quad 2H^2O \quad = \quad \underset{\text{Mellitimide.}}{C^4HNO^2}$$

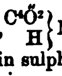
and **euchroïc acid**, which is a mellitamic acid, derived from an acid trimellitate of ammonium by abstraction of 4 at. water:

$$\underset{\text{Acid trimellitate of ammonium.}}{C^{12}H^4(NH^4)^2O^{12}} \quad - \quad 4H^2O \quad = \quad \underset{\text{Euchroïc acid.}}{C^{12}H^4N^2O^8}$$

Mellitamide $(C^4O^2)''.H^4.N^2$, and **mellitamic acid**  $\left.\begin{matrix} H^2 \\ (C^4O^2)'' \\ H \end{matrix}\right\} \begin{matrix} N, \\ O \end{matrix}$ are obtained, according to Limpricht and Scheibler, by the action of ammonia on neutral mellitate of ethyl.

Paramide and euchroïc acid are obtained by heating neutral mellitate of ammonium to 150°–160° as long as ammonia continues to escape, and exhausting the residue with water. Paramide then remains undissolved, and the solution contains euchroate of ammonium.

Euchroïc acid has already been described (ii. 601).

Paramide or **Mellitimide**,  $\left.\begin{matrix} C^4\overset{\prime\prime}{O}{}^2 \\ H \end{matrix}\right\} N$, is a white amorphous powder, insoluble in water and in alcohol, but soluble in sulphuric acid, whence it is precipitated by water. When heated with water to 200° in a sealed tube, or boiled for some time with water, fixed alkalis, or ammonia, it is converted into acid mellitate of ammonium. By the action of alkalis restricted to a shorter time, it is transformed into euchroïc acid:

$$\underset{\text{Paramide.}}{3C^4HNO^2} \quad + \quad 2H^2O \quad = \quad \underset{\text{Euchroïc acid.}}{C^{12}H^4N^2O^8} \quad + \quad NH^3.$$

An ammoniacal solution of paramide, mixed with nitrate of silver, forms a gelatinous precipitate, whose composition (at 150°) agrees best with the formula

$C^8H'^4Ag(NH^3Ag)N^2$; at 200° it gives off ammonia, and then contains a quantity of silver, corresponding nearly with the formula of argento-paramide, C^4AgNO^2.

Paramic acid.—This name is given by Schwarz to a white crystalline precipitate obtained by dropping an ammoniacal solution of paramide into hydrochloric acid. It is sparingly soluble in boiling water, and gives with zinc the reaction of euchroïc acid. Its ammoniacal solution is converted by boiling with mellitate of ammonium. Schwarz found in it (at 179°) 47·25 per cent. carbon, 2·16 hydrogen, and 13·78 nitrogen; a result which may be approximately represented by the formula $C^{12}H^5N^3O^7$.

MELLITIC ANHYDRIDE. $C^4\overset{\prime\prime}{O}{}^2.O$.—This is probably the composition of the white substance, insoluble in water and in alkalis, produced by heating chloride of mellityl with mellitic acid, and treating the product with water.

MELLITIC ETHERS. *Ethyl-mellitic acid*, $C^4H(C^2H^5)O^4$, is obtained by boiling mellitic acid for a considerable time with alcohol and sulphuric acid. On saturating with baryta-water, leaving the liquid to stand for some days in order that the excess of baryta may be precipitated as carbonate, then filtering to separate sulphate, mellitate, and carbonate of barium, a solution of ethyl-mellitate of barium is obtained, which, when evaporated in a vacuum over sulphuric acid, leaves the salt as an amorphous gummy mass, very soluble in water, and rotating on the surface of water like butyrate of barium. It is partly decomposed by drying at 100°. Its solution does not precipitate other metallic salts. (Erdmann and Marchand, J. pr. Chem. xliii. 129.)

Neutral Mellitate of Ethyl, $C^4(C^2H^5)^2O^4$, is obtained, according to Limpricht and Scheibler (*Limpricht's Lehrb. d. org. Chemie*, p. 1095), as a viscid liquid, by the action of iodide of ethyl on mellitate of silver. Kraut (Jahresb. 1863, p. 281) by the same reaction, obtained the *neutral mellitates of methyl*, *ethyl*, and *amyl*, the two former crystallised. H. Müller (*Kekulé's Lehrb. d. org. Chem.* p. 405) obtained the ethers of mellitic acid by the action of chloride of mellityl on the corresponding alcohols. The methylic ether thus obtained was crystallised; the ethylic ether liquid.

According to Limpricht and Scheibler, mellitate of ethyl treated with aqueous ammonia immediately produces a crystalline precipitate of mellitamide, $(C^4O^2)''.H^4.N^2$, and the solution, when evaporated, yields mellitamate of ammonium, $\left.\begin{array}{c}H^3\\(C^4O^2)''\\NH^4\end{array}\right\}\begin{array}{l}N\\O\end{array}$.

MELLITYL, CHLORIDE OF. $(C^4O^2)''.Cl^2$.—Obtained, together with hydrochloric acid and oxychloride of phosphorus, by heating mellitic acid with pentachloride of phosphorus. It is a crystalline non-volatile solid, which with *water* forms mellitic acid; with *alcohols*, mellitic ethers; and with *mellitic acid*, mellitic anhydride. (H. Müller, *loc. cit.*)

MELLONE. (Liebig, Ann. Ch. Pharm. x. 4; xxx. 149; l. 337; lvii. 93; lviii. 227; lxi. 262.—L. Gmelin, *ibid.* xv. 252.—Völckel, Pogg. Ann. lviii. 151; lxi. 375.—Gerhardt, Compt. Chim. 1845, p. 24, and 1850, p. 104; *Traité*, i. 473.—Laurent and Gerhardt, Ann. Ch. Phys. [3] xix. 85.)—A substance produced by the action of heat on various cyanogen-compounds; *e. g.*, pseudosulphocyanogen, melamine, melam, ammeline, ammelide, and chlorocyanamide. Liebig represents it by the formula C^3N^4 or C^6N^8; but according to the analyses of Völckel, and of Laurent and Gerhardt, the substance thus produced contains hydrogen (at least 1·5 per cent.), and may be represented by the formula $C^6N^9H^3$, the 3 at. H being replaceable by metals. Gerhardt designated this hydrated compound (Liebig's *crude mellone*) by the name hydromellone or hydromellonic acid, reserving the term mellone for the non-hydrogenous compound, which, according to Liebig, is produced by heating mellonide of mercury.

Mellone or hydromellone, heated with potassium or with iodide, bromide, or sulphocyanate of potassium, yields mellonide of potassium, which Liebig originally regarded as a compound of potassium with mellone, C^3N^4K or $C^6N^8K^2$: Laurent and Gerhardt, on the other hand, assigning to hydromellone the formula $C^6N^9H^3$, supposed that mellonide of potassium is produced by the substitution of 2 at. K for H, making the compound $C^6N^9HK^2$. Liebig, by later experiments (Ann. Ch. Pharm. xcv. 257), has come to the conclusion that his original formula of mellonide of potassium was incorrect, and that the true formula of the neutral mellonide is $C^9N^{13}M^3$.

Preparation of Hydromellone or Crude Mellone.—Liebig prepared this compound chiefly by heating dried pseudosulphocyanogen to low redness, or by gently heating a mixture of sulphocyanate of potassium and dry chloride of sodium in a stream of chlorine gas, and dissolving out the chlorides of potassium and sodium from the residue by water. According to Henneberg, it is best to heat the dry pseudosulphocyanogen, first in an open porcelain basin, and afterwards in a covered porcelain crucible; because, if it be heated in a retort, the sulphur which is given off flows back again, and causes the mellone to cake together. Too much heat must also be avoided, as the mellone then bakes together in hard lumps. The product thus obtained has a light-yellow colour with a tinge of grey; a grey or red-brown product may be regarded as a failure. As the complete expulsion of the sulphur from the preceding compounds requires strong ignition, and a large portion of the mellone is thereby decomposed, Laurent and Gerhardt prefer preparing it by heating chlorocyanamide till it ceases to give off hydrochloric acid and sal-ammoniac; or ammeline, as long as it gives off ammonia and water; or ammelide, as long as ammonia, cyanic, and cyanuric acids are evolved from it.

The product obtained by either of these processes is a loose, light-yellow, strongly staining powder, destitute of taste and smell. The following table exhibits its composition as determined by calculation and by analysis.

Formulæ and calculations, according to:

Liebig.			Laurent and Gerhardt.		
C^3	36	39·13	C^6	72	35·82
N^4	56	60·87	N^9	126	62·69
			H^3	3	1·49
C^3N^4	92	100·00	$C^6N^9H^3$	201	100·00

Analyses by Laurent and Gerhardt.

	a.	*b.*	*c.*	*d.*
C	35·73	35·8	36·4	36·0
N	62·50	62·4	61·9	62·2
H	1·77	1·8	1·7	1·8
	100·00	100·0	100·0	100·0

Analyses by Völckel.

	e.	*f.*	*g.*	*h.*	*i.*	*k.*	*l.*	*m.*	*n.*
C	31·63	36·01	37·02	32·17	36·52	36·31	35·57	32·49	35·07
N	. .	. .	. .	. .	. .	61·92	62·85		
H	1·42	1·75	1·91	2·03	1·71	1·77	1·58	1·89	2·09
						100·00	100·00		

Liebig based his formula on the combustion of crude mellone obtained from pseudosulphocyanogen with oxide of copper, which yielded 3 vol. carbonic anhydride to 2 vol. nitrogen, and on the decomposition of mellone by simple ignition, whereby he obtained 1 vol. nitrogen gas to 3 vol. cyanogen. Laurent and Gerhardt ignited their mellone for some time in a platinum crucible before analysing it: *a* was prepared from pseudosulphocyanogen, *b* from ammeline, *c* from ammelide, and *d* from chlorocyanamide. The crude mellone, *e*, *f*, *g*, analysed by Völckel, was obtained by variously long ignition of pseudosulphocyanogen prepared with nitric acid; *h*, with sulphocyanate of potassium and chlorine gas; *i* and *k*, from persulphocyanic acid; *l*, from Völckel's *poliene* (i.e. from the residue obtained by heating sulphocyanate of ammonium); *m* and *n*, from sulphocyanate of mercury.

It follows from the preceding analyses, that crude mellone, if the decomposition is stopped at a certain point, has a composition represented by the formula $C^6N^9H^3$, which is that of dicyanuramide, $\left.\begin{matrix}(C^3N^3)'''\\(C^3N^3)'''\\H^3\end{matrix}\right\}N^3$. The product when further heated still gives off ammonia and becomes continually richer in carbon. Whether it is possible, by continued heating, to expel the whole of the hydrogen in the form of ammonia, and thus to obtain a body having the composition of tricyanuramide $(C^3\overset{'''}{N^3})^3N^3$ (which is Liebig's original formula, C^3N^4, tripled,) is not yet distinctly made out; but it is probable that such is the case: at all events, the following formulæ show that melamine (cyanuramide) may, by loss of ammonia, be successively converted into melam, dicyanuramide, mellonide of hydrogen (according to Liebig's new formula), and ultimately into tricyanuramide:

$$\underset{\text{Cyanuramide.}}{2C^3N^6H^6} - NH^3 = \underset{\text{Melam.}}{C^6N^{11}H^9}.$$

$$\underset{\text{Melam.}}{C^6N^{11}H^9} - 2NH^3 = \underset{\text{Dicyanuramide.}}{C^6N^9H^3}.$$

$$\underset{\text{Dicyanuramide.}}{3C^6N^9H^3} - NH^3 = \underset{\text{Mellonide of hydrogen.}}{2C^9N^{13}H^3}.$$

$$\underset{\text{Mellonide of hydrogen.}}{C^9N^{13}H^3} - NH^3 = \underset{\text{Tricyanuramide.}}{C^9N^{12}}.$$

According to Liebig, pure mellone or tricyanuramide may also be obtained by heating mellonide of mercury till the evolved mixture of cyanogen and nitrogen gases is three-fourths absorbed by potash.

Decompositions.—1. Mellone heated in a closed vessel is gradually but completely resolved into a mixture of 1 vol. nitrogen gas and 3 vol. cyanogen (Liebig):

$$C^3N^4 = 3CN + N.$$

According to Völckel, it is resolved hereby into nitrogen, cyanogen, and hydrocyanic acid:

$$C^6N^9H^3 = 3CNH + 3CN + N^3.$$

When mellone obtained from ammelide or chlorocyanamide is ignited in a tube, it disappears completely, giving off vapours which smell of ammonia and hydrocyanic acid, and deposit first a red, then a yellow, and lastly a red-brown sublimate. The sublimate gives off ammonia when treated with potash, and precipitates nitrate of silver. The gaseous mixture evolved at the same time contains a gas (ammonia) which is absorbed by hydrochloric acid, another (cyanogen) which is absorbed by potash, and a non-absorbable gas (nitrogen), the relative quantities of the three being at the beginning of the experiment =9 : 51 : 40, and at the end =10 : 30 : 60. (Laurent and Gerhardt.)

2. Mellone heated in dry *chlorine gas* forms a white volatile substance having a powerful odour, and attacking the eyes very strongly.—3. Mellone dissolves gradually in boiling *nitric acid*, continually giving off a gas which contains very little or no nitric oxide, and is resolved into ammonia and cyanylic acid (ii. 294), which crystallises in long needles:

$$C^3N^4 + 3H^2O = C^3N^3H^3O^3 + NH^3. \quad \text{(Liebig.)}$$

Or,

$$C^6N^9H^3 + 6H^2O = 2C^3N^3H^3O^3 + 3NH^3. \quad \text{(Laurent and Gerhardt.)}$$

4. Mellone dissolves in strong *sulphuric acid*, with evolution of ammonia; water added to the solution throws down a white substance different from mellone.

5. Crude mellone heated with *potassium*, or with *iodide*, *bromide*, or *sulphocyanate of potassium*, is converted into mellonide of potassium.

6. With a cold solution of *caustic potash*, it forms mellonide of potassium, which at the boiling heat is converted, with evolution of ammonia and formation of ammelide, into cyamelurate of potassium (ii. 187):

$$\underset{\text{Mellonide of potassium.}}{2C^9N^{13}K^3} + 9H^2O = 3NH^3 + \underset{\text{Ammelide.}}{C^6N^9H^9O^3} + \underset{\text{Cyamelurate of potassium.}}{2C^6N^7K^3O^3}. \quad \text{(Liebig.)}$$

MELLONHYDRIC ACID. See the next article.

MELLONIDES. $C^6N^9M^3$, according to Gerhardt; $C^9N^{13}M^3$, according to Liebig's latest experiments (Ann. Ch. Pharm. xcv. 257). Mellonide of potassium is obtained, as already observed, by the action of potassium, or of iodide, bromide or sulphocyanate of potassium, on crude mellone. This and the corresponding salts of sodium and ammonium are soluble in water; the other mellonides are insoluble or sparingly soluble, and are obtained by precipitation. The sodium- and ammonium-salts are obtained by decomposing mellonide of barium with carbonate of sodium or of ammonium.

Mellonide of Ammonium crystallises in needles like the potassium-salt: it contains water of crystallisation.

Mellonide of Barium is obtained by treating the solution of the potassium-salt with chloride of barium, as a white precipitate which dissolves in a large quantity of boiling water. The saturated solution deposits the salt in transparent, shortened needles containing 20·87 per cent. water of crystallisation, which it gives off at 120°.

Mellonide of Calcium, obtained in like manner, is more soluble in boiling water than the barium-salt. The crystals contain 18·05 per cent. water, which they give off at 120°.

The following are obtained as precipitates: *mellonide of cadmium*, white; *chromium*, bluish-white; *cobalt*, peach-blossom-coloured; *copper*, parrot-green; *gold*, whitish-yellow.

Mellonide of Hydrogen. Mellonhydric or *Hydromellonic acid*, $C^9N^{13}H^3$.—By mixing a warm solution of mercuric chloride with mellonide of potassium, a fine-grained, dazzling white precipitate of mellonide of mercury is obtained, which, after washing, dissolves in dilute hydrocyanic acid, even in the cold. Sulphydric acid passed through this solution throws down all the mercury in the form of sulphide; and after driving off the hydrocyanic acid by a gentle heat, there remains an aqueous solution of hydromellonic acid, which has a strong acid taste and reaction, mixes with alcohol without turbidity, expels carbonic acid from carbonates with effervescence, and yields, when neutralised with potash, crystallised mellonide of potassium, exhibiting all the properties of the original salt (Liebig). L. Gmelin prepared the acid by decomposing the lead or copper salt with sulphydric acid.

When a solution of hydromellonic acid is evaporated, in vacuo or in the air, either at ordinary or at higher temperatures, it deposits white films or flakes, and leaves a somewhat crystalline residue, which redissolves but partially in cold water. The acid is not, however, completely decomposed under these circumstances; but the portion soluble in water still yields a certain quantity of mellonide of potassium when saturated with potash and mixed with alcohol. (Liebig.)

Mellonides of Iron.—The *ferric salt* is a dark-yellow precipitate; the *ferrous salt*, a white precipitate with greenish reflex.

Mellonide of Lead is a white precipitate which, after drying in the air, gives off 14·1 per cent. water when heated in a bath of chloride of calcium. The air-dried salt gives, according to L. Gmelin's analysis, 42·45 per cent. lead, agreeing nearly with the formula $2C^9N^{13}Pb^3.15H^2O$, which requires 42·58 per cent.

Mellonide of Magnesium is deposited, after some time, in small interlaced needles, from a mixture of mellonide of potassium and sulphate of magnesium.

Mellonide of Manganese is a white precipitate.

Mellonides of Mercury.—The *mercuric salt* is a white precipitate deposited on cooling from a boiling mixture of the solutions of mellonide of potassium and mercuric chloride: if the solutions are mixed cold, the precipitate contains potassium. The salt when heated first gives off nitrogen, cyanogen, and hydrocyanic acid; then nitrogen and cyanogen, in the proportion of 1 vol. of the former to 3 vol. of the latter. (Liebig.)

The *mercurous salt*, also obtained by precipitation, forms thick white flocks.

Mellonide of Platinum is a brownish-yellow precipitate.

Mellonides of Potassium.—Three of these salts have been obtained, viz the neutral salt, $C^9N^{13}K^3$, and the two acid salts, $C^9N^{13}HK^2$ and $C^9N^{13}H^2K$.

a. Neutral mellonide of potassium is obtained in many reactions besides those above mentioned (p 875), viz. by the action of amidated compounds of cyanogen on potassium-salts; by the action of sulphocyanates on potassium-salts; and by the decomposition of sulphocyanate of potassium under particular circumstances. When, for example, crude mellone (or calcined melam, &c.) is added to fused sulphocyanate of potassium, mellonide of potassium is produced, with evolution of sulphide of carbon, not only from the mellone, but also from the elements of the sulphocyanate. Again, when sulphocyanate of copper is added to melting sulphocyanate of potassium, sulphide of carbon is evolved, and mellonide of potassium remains mixed with metallic sulphide. Mellonide of potassium is also formed by heating sulphur with ferrocyanide of potassium (*e. g.* when the mixture used for preparing sulphocyanate of potassium is too strongly heated), its formation being due to the mutual action of the sulphocyanates of potassium and iron formed in the first instance. All these modes of formation of mellonide of potassium from sulphocyanates become intelligible on observing that a sulphocyanate contains the elements of sulphide of carbon, a metallic sulphide, and a mellonide, thus:

$$\underset{\text{Sulphocyanate.}}{13CNSM} = \underset{\text{Mellouide.}}{C^9N^{13}M^3} + 5M^2S + 4CS^2.$$

Preparation of Mellonide of Potassium.—a. From the *Sulphocyanate.* The preparation is considerably facilitated by the presence of a metal capable of taking up a portion of the sulphur which is set free as sulphide of carbon. The following processes are recommended by Liebig (Ann. Ch. Pharm. xcv. 257):

1. With *Antimonious chloride* (*butter of antimony*).—7 pts. of sulphocyanate of potassium are fused in a wide and deep porcelain crucible till the whole runs quietly and without frothing, and 3 pts. of recently-prepared butter of antimony then added by small portions. Strong intumescence then takes place, accompanied by brisk evolution of sulphide of carbon, which breaks out in flames, and must be extinguished by covering the crucible with a shallow dish; and a red-brown, porous mass is obtained, which must be pulverised and heated, with constant stirring, in an iron crucible, till part of the resulting sulphide of antimony melts in the softened pulpy mass, and collects at the bottom. The mass is then immediately dissolved in boiling water; the filtrate boiled with hydrated oxide of lead as long as the oxide turns black, to remove sulphide of potassium and dissolved sulphide of antimony; and the liquid again filtered and left to cool, whereupon it generally solidifies to a crystalline magma of snow-white mellonide of potassium. This product is thrown on a filter, the liquid allowed to drain off, and the mass, without being washed, is wrapped up with the filter in unsized paper, and placed over-night between two bricks, which are gradually

loaded with weights. The mass, when dry, is again dissolved in hot water, and the same process repeated. At the third crystallisation, the hot filtered liquid is mixed with a small quantity of alcohol, till a faint transient turbidity makes its appearance. The crystalline magma which settles down is washed with alcohol after the mother-liquor has drained off, till a drop of the liquid which runs off no longer reddens sesquichloride of iron, and therefore no longer contains sulphocyanate of potassium.—2. The chloride of antimony used in this process may, with equal advantage, be replaced by *chloride of bismuth*. This compound is prepared by passing chlorine gas over commercial bismuth, heated in a tube of hard glass, which is bent half an inch upwards at one end, then again downwards, and lies horizontally in a combustion furnace; the chloride of bismuth, which distils over, is purified from the chlorides of other metals by rectification in the same apparatus. Before being used, it is again melted, pulverised while still hot after solidification, and the powder added to the fused sulphocyanide. The proportions used are 1 pt. of bismuth-chloride to 2 pts. sulphocyanate of potassium; with a larger proportion of the former the mass will not melt.

b. From *Melam.*—8 pts. of sulphocyanate of potassium are fused with 4 pts. of melam, previously slightly ignited, and added in successive small portions. The temperature must not be allowed to rise too high; if the gas-bubbles which rise from the melted mass do not burn with a blue flame (sulphide of carbon), but with a red colour, indicating the formation of cyanogen, the heat must be moderated.

Pure mellonide of potassium forms soft, white, very slender interlaced needles, having a silky lustre, and scarcely distinguishable in appearance from sulphate of quinine.—1 pt. of the salt dissolves in 37·4 pts. of water at ordinary temperatures, and in a much smaller quantity of hot water: it is insoluble in alcohol; crystallises with difficulty, even from a solution saturated while warm, but very easily on addition of alcohol. Its solubility in cold water is greatly diminished by the presence of other salts. A warm saturated solution, which would stand for days after cooling without crystallising, instantly deposits crystals on addition of a few drops of solution of sulphocyanate of potassium.—The aqueous solution tastes as bitter as sulphate of quinine. In doses of a drachm, the salt exhibits no decided action on man or other animals, none at least which would distinguish it from other bitter substances. The crystals heated to 200° give off 18·06 per cent. (5 at.) water.

The composition of the anhydrous and crystallised salts, as determined by Liebig, is given in the following table:—

	Anhydrous.		Liebig.
C^9 . . .	108·0	26·50 . .	26·12
N^{13} . . .	182·0	44·65 . .	44·38
K^3. . .	117·6	28·85 . .	28·72
	407·6	100·00	99·22

	Crystallised.		Liebig.
$C^9N^{13}K^3$.	407·6	81·91	
$5H^2O$ . .	90·0	18·09 . .	18·06
$C^9N^{13}K^3.5H^2O$	497·6	100·00	

The dried salt burnt in a stream of oxygen yielded only 0·06 per cent. water: now, if it contained 1 at. hydrogen to 2 at. potassium, according to Gerhardt's formula, $C^6N^9HK^2$, it should have yielded 2·19 per cent. water; it may therefore be concluded that the salt does not contain hydrogen.

Neutral mellonide of potassium, boiled with hydrochloric acid, yields sal-ammoniac, chloride of potassium, and cyanuric acid. Boiled with nitric acid, it yields cyanylic acid. By continued boiling with potash, it gives off ammonia, and yields, first ammelide and cyameluric acid, then melanuric acid, and finally cyanuric acid (p. 876).

β. Soluble Acid salt. $C^9N^{13}HK^2.3H^2O$.—Obtained by mixing a warm saturated solution of the neutral salt with an equal volume of strong acetic acid. It crystallises from this mixture in oblique rhombic laminæ, which effloresce in a warm atmosphere. When boiled with water, it is resolved into the neutral salt *a*, and the insoluble acid salt *b*. The crystals, after drying in the air, give off 13·03 per cent. water (3 at. = 12·73 per cent.). The salt, dried at 150°, gave by analysis 28·75 per cent. carbon, 0·43 hydrogen, and 21·13 potassium; the formula $C^9N^{13}HK^2$ requiring 29·23 carbon, 49·28 nitrogen, 0·27 hydrogen, and 21·22 potassium. (Liebig.)

γ. Insoluble Acid salt. $C^9N^{13}H^2K$.—This salt separates in the form of a white, chalky precipitate, on pouring a moderately dilute solution of neutral mellonide of potassium into warm dilute hydrochloric acid. It is insoluble in cold and sparingly soluble in boiling water; the solution has a strong acid reaction; easily soluble in a solution of acetate of potassium. It gave by analysis 31·97 per cent. carbon, 0·76 hydrogen, and 11·93, potassium; the formula requiring 32·61 per cent. carbon, 54·99 nitrogen, 0·60 hydrogen, and 11·84 potassium.

Mellonide of Silver, $C^9N^{13}Ag^3$, is obtained as a white precipitate by mixing a boiling solution of neutral mellonide of potassium with nitrate of silver. It contains, according to the mean of Liebig's analyses, 17·48 per cent. carbon, 29·54 nitrogen, and 52·48 silver (= 99·50), the formula requiring 17·59 carbon, 29·64 nitrogen, and 52·77 silver (= 100).

Laurent and Gerhardt found in this salt 17·01 to 17·8 per cent. carbon, 52·2 silver, and 0·4 to 0·5 hydrogen; whence they deduced the formula $C^6N^9HAg^2$, requiring 17·3 C, 52·0 Ag, and 0·2 H. Liebig, however, by burning the salt in a stream of oxygen, obtained, in two experiments only 0·4 and 0·3 per cent. water; whereas, according to the latter formula, the quantity of water should be 2·17 per cent., or about six times as great as that actually obtained. Hence it may be inferred that the salt does not contain hydrogen.

Mellonide of Sodium, obtained by decomposing the barium-salt with carbonate of sodium, crystallises in white silky needles, moderately soluble in water, insoluble in alcohol.

Mellonide of Strontium is more soluble in water than mellonide of barium; its solution, saturated at the boiling heat, solidifies, on cooling, to a magma composed of needles.

Mellonide of Zinc is a white precipitate.

MELONEMETIN. An emetic principle contained, according to Torosiewicz, in the root of the melon (*Cucumis Melo*). See CUCUMIS (ii. 172).

MELOPSITE. A yellowish- or greenish-white lithomarge from Neudeck in Bohemia. Hardness = 2 to 3. Specific gravity = 2·5 to 2·6. (Breithaupt.)

MENACCANITE. Titaniferous iron. (See TITANATES).

MENAPHTOXIMIDE. } See NAPHTHYLAMINE, DERIVATIVES OF.
MENAPHTHYLAMINE. }

MENDIPITE. An oxychloride of lead, Pb^3ClO, found on the Mendip Hills in Somersetshire (p. 556).

MENEGHINITE. A sulphide of lead and antimony, $4Pb^2S.Sb^2S^3$, occurring, with Boulangerite and Jamesonite, at Bottino in Tuscany, generally in compact fibrous forms, but sometimes in distinct trimetric crystals, exhibiting the faces $\infty\breve{P}\infty$ and ∞P; cleavable parallel to $\infty\breve{P}\infty$ and oP (Q. Sella, Jahresb. 1862, p. 712). Hardness = 2·5. Very lustrous. Contains, according to Bechi's analysis (Sill. Am. J. [2] xiv. 60), 17·52 per cent. sulphur, 19·28 antimony, 59·21 lead, 3·54 copper, and 0·34 iron (= 99·89).

MENGITE. A mineral containing zirconia, ferric oxide, and titanic acid, occurring in granite-veins in the Ilmen Mountains. It forms short trimetric prisms, often terminated by four-sided pyramids. $a : b : c = 0·8285 : 1 : 0·8669$. Angle $\infty P : \infty P = 100° 28' : oP : \breve{P}\infty = 133° 42'$. No distinct cleavage. Hardness = 5 to 5·5. Specific gravity = 5·48. The crystals are iron-black, with submetallic lustre, subvitreous on the fractured surface. Streak chestnut-brown. Fracture uneven. Infusible before the blowpipe, but becomes magnetic. Greenish-yellow clear glass with phosphorus-salt in the outer flame; yellowish-red in the inner, deepened by adding tin. Manganese reaction with carbonate of sodium.

This mineral is called ilmenite by Brooke; and the name mengite is applied by that mineralogist to monazite.

MENILITE. A brown opaque variety of opal, occurring in compact reniform masses, occasionally slaty.

MENISPERMIC ACID. A doubtful acid, said by Boullay to exist in the seeds of *Menispermum Cocculus*, and to be obtained by evaporation of the alcoholic mother-liquor from which picrotoxine has crystallised out. It is described as crystalline, tasteless, sparingly soluble in water, capable of reddening litmus, and forming crystallisable salts with alkalis. Neither Casaseca nor Pelletier was able to obtain this acid in the manner described by Boullay.

MENISPERMINE. An alkaloïd discovered by Pelletier and Couerbe (Ann. Ch. Phys. [2] liv. 178) in the seeds of *Menispermum Cocculus*, in which it is accompanied by paramenispermine and picrotoxine.

To extract the menispermine, the alcoholic extract of the seeds is first treated with cold water, then exhausted with hot acidulated water; the brown solution is precipitated by an alkali; and the precipitate is exhausted with very weak acetic acid, which leaves a brown-black mass undissolved. Or the seeds may be made up into a heap, and exhausted with alcohol of specific gravity 0·833; the alcohol distilled off; the residue boiled with water; and the liquid filtered at the boiling heat; it then, on cooling, deposits crystals of picrotoxine, especially if a small quantity of acid has been added. The part insoluble in boiling water is then treated with acidulated water, and precipitated by an alkali; a granular precipitate is thereby formed, from which alcohol extracts a peculiar yellow substance; and the residue is finally dissolved in ether, which deposits menispermine in the crystalline form. The ether leaves undissolved a viscous substance, which may be dissolved in absolute alcohol; and the solution, evaporated at 45°, ultimately yields crystals of paramenispermine.

Menispermine crystallises in prisms terminated by pyramidal faces. It is white, melts at 120°, and decomposes at a higher temperature. It does not appear to be poisonous. It is insoluble in *water*, but soluble in *alcohol* and *ether*, which deposit it in the crystalline state. It contains (mean of four analyses) 71·80 per cent. carbon, 8·01 hydrogen, 8·57 nitrogen, and 10·53 oxygen; whence Pelletier and Couerbe deduce the formula $C^{18}H^{12}NO^2$.

Menispermine dissolves easily in dilute *acids*. Hot strong *nitric acid* converts it into oxalic acid, and a yellow resinous substance.

Sulphate of menispermine crystallises in prismatic needles, containing 15 per cent. water and 6·87 per cent. sulphuric anhydride. It melts at 165°, and at a higher temperature reddens slightly and gives off sulphydric acid.

Paramenispermine has the same composition as menispermine. It melts at 250°, and volatilises in white vapours, which condense like snow on cold bodies. It is insoluble in *water*, sparingly soluble in *ether*, easily soluble in boiling *alcohol*. It dissolves also in dilute *acids*, but without neutralising them or forming definite salts.

MENTHENE. $C^{10}H^{18}$. (Walter, Ann. Ch. Pharm. xxxii. 288.—Oppenheim, Chem. Soc. J. xv. 29.)—A hydrocarbon produced by the action of phosphoric anhydride (Walter), or chloride of zinc (Oppenheim), on menthol or peppermint camphor, $C^{10}H^{20}O$. It is also found among the products of the decomposition of chloride of menthyl by ethylate of sodium (Oppenheim). To prepare it, menthol is melted in a tubulated retort, and phosphoric anhydride is added by small portions till it is in slight excess. The mass is then distilled, and the product is rectified by distillation over fresh portions of phosphoric anhydride.

Menthene is a transparent, very mobile liquid, having an agreeable odour and cooling taste. Boiling-point 163°. Specific gravity = 0·851 at 21°. Vapour-density, obs. = 4·93 to 4·95; calc. = 4·78. It is insoluble in water; forms a turbid mixture with a small quantity of *alcohol* or *ether*, a clear mixture with a larger quantity; dissolves with moderate facility in *wood-spirit*, very easily in *oil of turpentine*.

Menthene is scarcely, if at all, attacked by *potassium*; cold *sulphuric acid* has no action upon it; *nitric acid* ultimately converts it into an oily acid, soluble in water and in alcohol; with *chlorine* and *bromine* it forms substitution-products.

Bromomenthene. $C^{10}H^{17}Br$.—Bromine acts very violently on menthene, disengaging torrents of hydrobromic acid, and forming a number of very unstable substitution-products. By adding 2 at. bromine drop by drop to 1 at. menthene, monobromomenthene appears to be formed, the product treated with potash yielding the hydrocarbon $C^{10}H^{16}$ (Oppenheim):

$$C^{10}H^{17}Br + KHO = KBr + H^2O + C^{10}H^{16}.$$

Pentachloromenthene, $C^{10}H^{13}Cl^5$, is produced by the action of chlorine on menthene. Dry chlorine attacks menthene with great violence, hydrochloric acid being evolved, the liquid assuming first a green, then a yellow colour, and being ultimately converted into pentachloromenthene, which is a yellow syrupy liquid heavier than water. It dissolves at ordinary temperatures in *alcohol* and *wood-spirit*, more easily in *ether* and *oil of turpentine*. Strong *sulphuric acid* colours it deep red.

MENTHOL. $C^{10}H^{20}O = \left.\begin{matrix}C^{10}H^{19}\\H\end{matrix}\right\}O$. *Menthylic alcohol. Hydrate of Menthyl. Camphor* or *Stearoptene of Peppermint-oil.* (L. Gmelin, *Handbuch*, Aufl. 3, ii. 408.—Dumas, Ann. Ch. Pharm. vi. 252.—Blanchet and Sell, *ibid.* vi. 293.—Walter, *ibid.* xxxii. 288.—Kane, Phil. Mag. xvi. 418.—Laurent, Rev. scient. xiv. 341.—Oppenheim, Chem. Soc. J. xv. 24). The essential oil of peppermint, when kept for a long time, or cooled to very low temperatures, deposits this substance in crystals. American peppermint-oil yields this deposit at temperatures near 0°. This camphor is now imported in large quantities from Japan, in small, white, fragrant, prismatic crystals, resembling sulphate of magnesium, which salt is in fact used for adulterating the Japanese camphor, sometimes to the amount of 10 to 20 per cent.

The camphor from American oil of peppermint melts at 36·5° (Gmelin); at 25° (Dumas); 27° (Blanchet and Sell); 34° (Walter); the Japanese camphor melts at 36°, and volatilises without decomposition at 210° (Oppenheim). Vapour-density, obs. = 5·62; calc. = 5·41. It is lævo-rotatory. $[\alpha] = -59·6°$ [? for the transition-tint.]

It is but slightly soluble in *water*, but imparts to that liquid a strong smell and taste. It is very soluble in *alcohol*, *ether*, *sulphide of carbon*, and *oils*, both fixed and volatile; insoluble in aqueous *alkalis*. From an alcoholic soda-solution, it crystallises in long needles. It is dissolved by a current of *sulphurous anhydride*, or *hydrochloric acid gas*, but the acid passes off on evaporation, leaving the menthol unaltered. Concentrated acids, especially *nitric*, *sulphuric*, *hydrochloric*, *formic*, *acetic*, and *butyric acids*, dissolve it freely; and from these solutions it is precipitated by water and by alkalis, as an oil, which soon solidifies, and then exhibits the original properties of the camphor.

Heated with strong hydrochloric to 100° for a considerable time, it is transformed into chloride of menthyl, $C^{10}H^{19}Cl$. The same compound is formed by the action of *pentachloride of phosphorus*:

$$C^{10}H^{20}O + PCl^5 = PCl^3O + HCl.C^{10}H^{19}Cl.$$

With *iodide* and *bromide of phosphorus*, it yields iodide and bromide of menthyl; *hydriodic acid* also acts upon it at 200°, forming iodide of menthyl.

Heated with concentrated *acetic acid* in a sealed tube, it is converted into acetate of menthyl, $\left.\begin{matrix}C^{10}H^{19}\\C^2H^3O\end{matrix}\right\}O$. With *butyric acid* it forms, in like manner, butyrate of menthyl, $\left.\begin{matrix}C^{10}H^{19}\\C^4H^7O\end{matrix}\right\}O$.

These reactions show that peppermint-camphor is an alcohol containing the radicle $C^{10}H^{19}$ (menthyl); it is homologous with allylic alcohol, C^3H^6O, and isologous with campholic alcohol or camphol, $C^{10}H^{18}O$ (i.e. differs from the latter by 2 at. H): hence the names menthylic or mentholic alcohol, and menthol applied to it.

Sodium acts very energetically on menthol, with evolution of hydrogen and formation of a substitution-product, which is a white, vitreous, transparent mass, becoming brown on exposure to the air, insoluble in water, but soluble in absolute alcohol and iodide of ethyl. The latter body acts on the sodium compound; but the action is complicated, and does not appear to give rise to the formation of a compound ether, as with most sodium-alcohols.

Menthol is dehydrated by *phosphoric anhydride* or *chloride of zinc*, yielding menthene.

MENTHYL. $C^{10}H^{19}$. The radicle of menthylic alcohol, &c.

Acetate of Menthyl, $\left.\begin{matrix}C^{10}H^{19}\\C^2H^3O\end{matrix}\right\}O$, prepared by heating menthol with strong acetic acid to 120° in a sealed tube for ten or twelve hours, then washing with carbonate of sodium, and drying over chloride of calcium, is a light oil which boils without decomposition between 222° and 224°. It is highly refractive, and lævo-rotatory; $[\alpha] = -114°$. It is not decomposed by water, or by cold solutions of the alkalis, or by baryta, but when heated to 120°, with an alcoholic solution of soda, it is completely resolved into sodic acetate and menthol. (Oppenheim, Chem. Soc. J. xv. 26.)

Butyrate of Menthyl, $\left.\begin{matrix}C^{10}H^{19}\\C^4H^7O\end{matrix}\right\}O$, is prepared by heating menthol with butyric acid, in a sealed tube, to 200° for thirty hours; then distilling and collecting the portion which passes over between 230° and 240°. Rotatory power $[\alpha] = 88.8°$ nearly.

Chloride of Menthyl, $C^{10}H^{19}Cl$. Obtained by treating menthol with pentachloride of phosphorus (Walter), or with concentrated hydrochloric acid for a week, at 100°, or for twenty-four hours at 120° (Oppenheim). It is a very pale yellow liquid, lighter than water, heavier than alcohol, and having an odour like that of mace; boils at about 204°, decomposing and turning brown at the same time. It is slightly soluble in water, more soluble in alcohol. It is rapidly decomposed by potassium, but strong alcoholic potash has no action upon it, even at the boiling heat. (Walter.)

Bromide and *Iodide of Menthyl* are obtained by the action of bromide and iodide of phosphorus on menthol; the latter also by the action of strong hydriodic acid. Both compounds are decomposed by distillation. (Oppenheim.)

MENYANTHIN. $C^{22}H^{36}O^{11}$.—A bitter substance discovered by Brandes in buckbean (*Menyanthes trifoliata*), and further examined by Kromayer (Zeitschr. Anal. Chem. i. 15; Jahresb. 1861, 747). It may be prepared by a process similar to that described for the extraction of marrubiïn (p. 854). It is thus obtained as a nearly colourless resinous mass, which, after drying over sulphuric acid, is amorphous, friable, permanent in the air, neutral, and has an intense and purely bitter taste. It begins to soften between 60° and 65°, becomes quite fluid at 115°, and solidifies on cooling to a hard yellowish transparent mass. At higher temperatures it gives off first aromatic, then pungent vapours, smelling like oil of mustard. It dissolves sparingly in cold *water*, easily in hot water and in *alcohol*, but is insoluble in *ether*; *alkalis* dissolve it apparently without alteration. It dissolves with various shades of colour in strong *sulphurous*, *nitric*, and *hydrochloric acids*. The aqueous solution is not precipitated by *metallic salts*, but form with *gallotannic acid* a precipitate having the composition $C^{40}H^{62}O^{23} = C^{28}H^{38}O^{11}.2C^6H^{12}O^6$. Menyanthin is isomeric with pinipicrin, which it also resembles in many of its properties. (Kromayer.)

The name menyanthin has also been applied to a neutral amylaceous substance contained in buckbean; probably identical with inulin (p. 277).

MENYANTHOL. An oily body, obtained by distilling menyanthin with dilute sulphuric acid. The residue in the retort contains fermentable sugar. It is heavy, colourless, smells like bitter almond oil; has a faint acid reaction, and reduces an ammoniacal silver solution. (Kromayer.)

MERCAPTANS. Sulphydrates of the alcohol-radicles, *e.g.*, sulphydrate of ethyl $\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}S$. (See the several Alcohol-radicles, *e.g.*, ETHYL, ii. 547.)

MERCAPTIDES. Compounds formed by the substitution of metals for hydrogen in the mercaptans.

MERCURAMINES AND MERCURAMMONIUMS. See MERCURY-BASES, AMMONIACAL.

MERCURIALIS. The ash of *Mercurialis perennis* (the herb together with the fruit) has been analysed by N. Reitler (Jahresb. 1860, p. 543). The air-dried plants yielded 84·4 per cent. dry residue at 100°. The ash amounted to 11·5 per cent. of the air-dried plant, and 13·09 per cent. of the plant dried at 100°. It contained 27·14 per cent. CO^2, 9·18 Cl, 0·98 SO^3, 0·84 SiO^2, 2·74 P^2O^5, 0·27 Fe^4O^3, 31·57 Ca^2O, 5·59 Mg^2O, 14·35 K^2O, 6·84 Na^2O, with a trace of copper (loss 0·50).

MERCURIC AMYLIDE, ETHIDE, &c. See MERCURY-RADICLES, ORGANIC.

MERCURIUS. This term was applied by the alchemists to all volatile substances: thus quicksilver was called *Mercurius communis*; alcohol, *Mercurius vegetabilis*. At present it is applied only to quicksilver.

Mercurius dulcis. Syn. with calomel (p. 893).

Mercurius cinereus Blackii, blackish-grey mercurial precipitate, is a mixture of mercurous carbonate with *Mercurius solubilis Hahnemanni*, obtained by precipitating mercurous nitrate with carbonate of ammonium.

Mercurius cinereus Moscati, the *Mercurius solubilis* of the Swedes, consists of black mercurous oxide, obtained by decomposing calomel with caustic potash or soda.

Mercurius cinereus Saunderi. An almost obsolete pharmaceutical preparation consisting of chloride of mercurosammonium $(Hhg^3H^2N)Cl$, obtained by decomposing colomel with ammonia. (See MERCURY-BASES, AMMONIACAL.)

Mercurius phosphatus Fuchsii. An obsolete preparation obtained by precipitating a solution of mercury in nitric acid with phosphate of sodium.

Mercurius præcipitatus albus. *Hydrargyrum amido-bichloratum, Hydrargyrum amido-muriaticum, Hydrargyrum præcipitatum album, Mercurius cosmeticus, Calx hydrargyri alba, Lac mercuriale.—White precipitate.* Of this mercurial preparation there are two varieties, distinguished as fusible and infusible. The former consists of *chloride of mercurammonium*, HgH^3NCl or $Hhg''H^6N^2Cl^2$, obtained by precipitating ammonio-mercuric chloride with potash, or by dropping a solution of mercuric chloride into a solution of sal-ammoniac mixed with ammonia, as long as the precipitate first formed is redissolved; the latter, of *chloride of dimercurammonium* Hg^2H^2NCl, or $Hhg''H^2NCl$, obtained by adding ammonia to mercuric chloride.

Mercurius præcipitatus ruber. *Oxydum hydrargyricum.* Mercuric oxide obtained either by oxidising mercury in contact with the air at the boiling heat, or by heating it with nitric acid. The product obtained by the first of these methods is also called *Mercurius præcipitatus per se* (see p. 907).

Mercurius solubilis Hahnemanni. *Hydrargyrum oxydulatum nigrum. Nitrus ammonicus cum oxydo hydrargyrico.* Basic nitrate of mercurosammonia. See MERCURY-BASES, AMMONIACAL.

Mercurius violaceus. A form of mercuric sulphide, obtained by triturating together 6 pts. melted flowers of sulphur, 6 pts. mercury, and 4 pts. sal-ammoniac, pulverising the cooled mass, subliming it in a flask, removing the upper white deposit, consisting of sal-ammoniac, and resubliming the lower, heavier sublimate three times. The upper part of the sublimate, thus obtained, is usually light and yellow; the lower heavy and violet. The latter, after it has been finely pounded and alcohol burnt upon it, constitutes *Mercurius violaceus.*

Mercurius vitæ. Powder of Algaroth (oxychloride of antimony, i. 327).

Mercurius vivus. Metallic mercury.

MERCURO-TETRETHYL-AMMONIUM. $C^8H^{19}HgN$. A base, the iodide of which is obtained, according to Sonnenschein, together with several other compounds, by the action of iodide of ethyl on *white precipitate* (ii. 535).

MERCURY. Synonymes: *Quicksilver, Hydrargyrum, Argentum vivum, Mercurius vivus.* Symbols and Atomic Weights: $Hg = 100$; Hhg'' or $\cancel{H}g'' = 200$.

This metal has been known from the earliest times; cinnabar was used as a pigment by the ancients; corrosive sublimate was known to the Arabians, and calomel to the alchemists.

Mercury is often found native, in globules disseminated through its ores; it occurs also combined with silver and with gold, in the form of amalgams; also as iodide and chloride, and very rarely as selenide; but the most abundant ore is the sulphide, or cinnabar, from which nearly all the mercury of commerce is obtained. Its most important mines are those of Idria in Illyria, and of Almaden in Spain. At Almaden it is found in veins, often nearly fifty feet thick, traversing micaceous schists of the older transition period; in Illyria it is disseminated in beds of grit, bituminous schist, or compact limestone of more recent date. It occurs also in the Bavarian Palatinate, at Horzowitz in Bohemia, at Schemnitz in Hungary, and a few other localities in Europe; on the Ural and Altai mountains; in China abundantly, and in Japan; at San Onofre, in Mexico; abundantly at Huanca Velica, in Southern Peru; in the province of Coquimbo, Chile; and forms extensive mines at New Almaden in California.

Preparation.—By distilling mercurial ores with lime, smithy-scales, or simply in contact with the air, so as to remove the sulphur by formation of sulphide of calcium, sulphide of iron, or sulphurous anhydride; partly also to remove chlorine. In the Bavarian Palatinate, a mixture of ore and lime is heated to redness in long cast-iron bottles, placed in nearly horizontal rows, one above the other in a long furnace, and provided with receivers. At Horzowitz, in Bohemia, a mixture of ore and smithy-scales is placed in iron dishes, which are attached one above the other by the centres of their bases to a vertical iron axis, and covered over with an iron receiver, closed at top, and dipping into water at bottom. The upper part of the receiver is surrounded by the furnace, and imparts its heat to the dishes, from which the mercury rises in vapour, and collects in the water contained in the trough. This process is called *Destillatio per descensum* At Idria, in Illyria, the quicksilver-ore, coarsely broken up, is laid upon a perforated stone arch, in a turret-shaped furnace, and after the apertures by which it is introduced have been stopped, heated to redness by flames made to play against the under surface of the arch. The sulphur is burnt by the air, which is admitted through channels constructed for the purpose; and the mixture of mercurial vapour, sulphurous acid, and smoke from the furnace, is made to pass through a horizontal channel constructed in the upper part of the furnace, then up and down through seven condensing chambers, and finally through a turret-shaped forge into the air. In the course of this long transit, the mercury condenses in the chambers, the floor of which, being inclined to one side, enables it to run out; it is then collected, and strained through coarse cloth. A similar process is followed at Almaden, in Spain, excepting that the vapours, instead of passing through condensing chambers, are made to traverse a series of tubes made up of cylinders, called *Aludels* (i. 149), open at both ends, and fitting one into the other. These are laid upon a surface, called the *Aludel-bath*, first descending a little, and then ascending, and finally open into the chimney. [For details and figures of all these forms of apparatus, and of an improved process suggested by Dr. Ure for performing the distillation in iron retorts, see *Ure's Dictionary of Arts*, &c., iii. 58]. Mercury is sent into the market, sometimes in leathern bags, sometimes in wrought-iron bottles, which are afterwards used in chemical laboratories for the preparation of potassium.

Purification from foreign metals.—1. The mercury is distilled either alone, or, better, under a thick layer of iron filings, in glass, earthen, or other retorts. A portion of the foreign metals is very apt to pass over with the mercury, either in the form of vapour or by spirting during the ebullition. The latter of these accidents is prevented by the coating of iron-filings. 2. By distilling the mercury with one-tenth of its weight of cinnabar, the sulphur of which retains the foreign metals. (Därfurt.)

3. By boiling the impure mercury for some hours with $\frac{1}{87}$ of its weight of mercurous nitrate dissolved in water, or with a small quantity of very dilute nitric acid, or by digesting it with either of these liquids in the cold, the mercury being placed in a shallow dish, so as to expose a large surface, and frequently agitated; or by agitating the mercury for some days with sulphuric acid—which must be stronger, as the mercury is more impure—till the acid no longer becomes turbid, or takes up any foreign substance (Branchi, Repert. Pharm. vi. 77).—4. Ulex (Ann. Ch. Pharm. lx. 210) agitates two pounds of mercury with half an ounce of solution of ferric chloride,

fine division, and the action on the foreign metals is accelerated by the formation of chloride of mercury, which collects between the drops. It is sufficient to agitate the mercury with the iron solution for ten minutes, and then wash it with water. The mercury, after drying, is easily reunited by the application of a gentle heat.—5. A small quantity of mercury may be speedily purified by placing it in a bottle with a little finely powdered loaf-sugar, the mercury not occupying more than one-fourth of the capacity of the bottle; the bottle is then closed and briskly agitated for a few minutes, after which the stopper is withdrawn, and fresh air blown into the bottle with a pair of bellows, and the agitation is repeated; this is done three or four times, and the mercury is then poured into a cone of smooth writing paper, having a pin-hole at its apex. The metal then runs through, leaving the pounded sugar mixed with the oxides of the foreign metals, and a considerable quantity of finely divided mercury.

Pure mercury should leave no residue when dissolved in nitric acid, evaporated and ignited; or when fused with sulphur and sublimed in a glass flask. When made to run down a gently-inclined surface, it should retain its round form, and *not drag a tail;* and when agitated in a bottle with dry air, it should not yield any black powder.

Properties.—Mercury freezes, according to Hutchins, at − 39·44°, undergoing considerable contraction, and forming a tin-white, ductile mass, crystallised in octahedrons and needles, capable of being cut with a knife, and exhibiting a granular fracture. At ordinary temperatures, it forms a very coherent but very mobile liquid, which adheres but slightly to glass, and has a density of 13·5592 (Karsten), 13·5886 at 4°, and 13·535 at 26° (Kupffer), 13·568 (Cavendish and Brisson), 13·575 (Fahrenheit), 13·613 at 10° (Biddle), 13·595 at 4° (Kopp), 13·596 (Regnault). For its specific heat see Heat (p. 30); rate of expansion (pp. 54-57); latent heat of fusion (p. 77).

Mercury remains unaltered when agitated for any length of time with oxygen gas, common air, hydrogen, nitrogen, nitrous oxide, nitric oxide, carbonic acid gas, or alcohol; but any foreign metals that may be mixed with it become oxidised by agitation in air or oxygen gas, producing a grey pulverulent mixture of the oxides of the foreign metals and finely divided metallic mercury. On the other hand, by agitation with water, ether, or oil of turpentine, or by trituration with sulphur, sulphide of antimony, sugar, grease, &c., even in vacuo, mercury is converted into a grey powder, *Æthiops per se*, consisting of small globules of the metal, which are separated by interposition of foreign matter, but run together again on its removal: this is called the *Extinction* or *Deadening of Mercury.* In well prepared grey mercurial ointment, the mercury forms nearly uniform globules, having a diameter between $\frac{1}{800}$ and $\frac{1}{1000}$ of a line, and not distinguishable by the naked eye (Ehrenberg, Pogg. xxiv. 40). The deadening of mercury was formerly attributed to oxidation. According to Bärensprung (J. pr. Chem. l. 21), some, at least, of the mercury in grey mercurial ointment is in the state of black oxide (the quantity being greater, the older the ointment), and this oxide, after the fat has been extracted by ether, may be dissolved out by water slightly acidulated with sulphuric acid.

Mercury boils, according to Crichton, at 346°; according to Dalton, at 349°; according to Heinrich, at 356°; according to Dulong and Petit, at 360°, and is thereby converted into a colourless vapour. Vapour rises, however, from mercury, even between + 15·5° and 27° (but not at − 6·7°), both in vacuo and in spaces filled with air, as shown by the silvering of gold-leaf, kept for two months in a vessel over mercury (Faraday, 7°). According to Karsten (Pogg. Ann. lxxi. 245), mercury at temperatures below 0°, gives off sufficient vapour to bring out the image on a Daguerreotype plate held over it. Brame (Instit. 1849, 403) finds that sulphur in the very finely divided utricular condition (*utricules de soufre*) in which it is first precipitated from the state of vapour, is a much more delicate test for the presence of mercurial vapour than gold-leaf. By means of this test, he finds that at 12° the vapour of mercury rises to a height of more than a metre—that even at 8°, it appears to have no limited atmosphere—that it rises, at ordinary temperatures, from amalgams and mercurial ointment—that in presence of air and sulphur-vapour, it diffuses, according to the same law as other gases—but that in presence of air and iodine-vapour, and of the vapour of iodide of mercury thereby produced, the law of diffusion appears to be different. (For the tension of mercury-vapour at different temperatures, see Heat, p. 94.)

The density of mercury-vapour, referred to air as unity, is 6·7 (Bineau, Compt. rend. xlix. 799). The theoretical density is 100 referred to hydrogen, or 6·933 referred to air, as unity, the molecule of the vapour containing 2 at. Hg (= 100) or 1 at. Hhg (= 200).

According to Wiggers (Pogg. Ann. 440), mercury is slightly soluble in boiling *water.* When twenty ounces of water are poured upon two ounces of mercury, and boiled down to ten ounces, the decanted liquid shows no particular reaction with sulphydric acid or stannous chloride; but on mixing it with ten drops of nitric acid, and evaporating, the residue exhibits a slight brown tint when treated with sulphydric acid. Anthon also (J. pr. Chem. xv. 153) found that water boiled with mercury for fifteen hours, and then decanted, was capable of silvering gold-leaf; and after evaporation with nitric acid, gave the characteristic reactions with sulphydric acid and stannous chloride. Paton and Favrot (J. Chim. méd. xiv. 306), in repeating the experiment of Wiggers with distilled water and with river-water, did not discover mercury in the water after evaporation with nitric acid: Girardin also (J. Chim. méd. ix. 283) found no mercury in water which had been boiled with that metal; he did not, however, mix it with nitric acid before evaporation. When water is poured upon mercury, boiled down to one-half, decanted, then left to stand for several days, again decanted, and thrown upon a thick paper filter, small quantities of mercury, sufficient to silver gold-leaf, remain on the filter; but the filtrate, when mixed with nitric acid and evaporated, shows no trace of mercury. Perhaps the quantity used in the experiment was too small; but, at all events, the experiment shows that the mere decantation adopted by Wiggers is not sufficient to separate the water from the mercury mechanically mixed with it; to decide the question completely, experiments should be made with large quantities of water. (L. Gmelin, *Handbook*, vi. 4.)

Hydrochloric acid, even when hot and concentrated, has no action upon mercury. *Nitric acid* slowly dissolves it in the cold; and, if the acid is in excess, converts it into neutral mercurous nitrate. When nitric acid is boiled with excess of mercury, the metal is converted into basic mercurous nitrate, which crystallises on cooling. If, on the other hand, the nitric acid is in excess, the whole of the mercury is converted into mercuric nitrate; mercury heated with excess of *nitromuriatic acid*, yields mercuric chloride and nitrate. Mercury is scarcely attacked by dilute *sulphuric acid*, but when heated with the concentrated acid, it is converted into solid mercuric sulphate, with evolution of sulphurous anhydride. If the sulphuric acid is small in quantity, and the heat is not raised quite to the boiling point, mercurous sulphate is obtained. *Chlorine gas* passed over gently heated mercury, converts it into mercuric chloride.

Mercury forms two series of compounds, viz., the mercurous compounds, in which it is hemi-atomic or monatomic, and the mercuric compounds, in which it is mono- or di-atomic, according as the smaller or larger atomic weight of the metal is adopted thus:

Mercurous chloride . .	Hg^2Cl	=	2.100	+	35·5	=	235·5
or	$HhgCl$	=	200	+	35·5	=	235·5
Mercurous oxide . .	Hg^4O	=	4.100	+	16	=	416
or	Hhg^2O	=	2.200	+	16	=	416
Mercuric chloride . .	$HgCl$	=	100	+	35·5	=	135·5
or	$H\overset{\prime\prime}{hg}Cl^2$	=	200	+	2.35·5	=	271
Mercuric oxide . .	Hg^2O	=	2.100	+	16	=	216
or	$H\overset{\prime\prime}{hg}O$	=	200	+	16	=	216

There are also several compounds into which mercury enters as a base or radicle belonging to the types ammonia and ammonium, *e.g.* bromide of mercurammonium $\left.\begin{matrix}Hg\\H^3\end{matrix}\right\}NBr$; chloride of tetramercurammonium, Hg^4NCl trimercuramine, Hg^3N is known in the free state.

MERCURY, ALLOYS or AMALGAMS OF. Mercury is capable of uniting with most other metals, forming compounds called amalgams, some of which are liquid, while others are solid. The solid amalgams appear to be for the most part of definite chemical constitution; while the liquid amalgams may be regarded in many instances as solutions of definite compounds in excess of mercury, inasmuch as when they are pressed between chamois leather, mercury containing but a small quantity of the other metal passes through, while a solid amalgam, frequently of definite atomic constitution, remains behind. Even in the solid amalgams, however, the affinity by which the two metals are held together is but feeble; for Joule has shown that many of those which contain equal numbers of atoms of their component metals may be partly decomposed by subjecting them to very strong pressure, part of the mercury being then forced out, and an amalgam containing a larger portion of the other metals remaining behind. In most instances also the formation of amalgams is attended with little or no contraction of volume; in the case of silver and copper, however, the contraction is considerable—and with tin, lead, and a few others, it is perceptible. The union of mercury with potassium and sodium is attended with considerable evolution of heat.

The methods of combining mercury with other metals are:

1. Bringing the mercury into direct contact with the other metal, either in the solid

state or finely divided, the action sometimes taking place at ordinary temperatures, sometimes requiring the assistance of heat.

2. The introduction of metallic mercury into the solution of a salt of the other metal, part of the mercury then passing into the solution and precipitating the other metal, which then unites with the rest of the mercury. In some cases the precipitation may be more easily effected by means of an amalgam of a highly electro-positive metal, sodium for example. A sodium-salt is then formed, and the other metal is precipitated on the mercury and unites with it.

3. The introduction of various metals into solutions of mercury-salts, copper for example. In the case of silver, gold, or platinum, which do not directly precipitate mercury from its solutions, the action must be assisted by immersing a piece of zinc or iron into the solution, and bringing it in contact with the other metal, so as to form a voltaic circuit: thus a drop of solution of mercuric chloride laid on a piece of gold will not amalgamate it; but if an iron wire or a key be placed in contact with the wetted surface of the gold, a white spot of amalgam is immediately formed at the point of contact.

4. By placing the metal to be amalgamated in contact with mercury and with a dilute acid, a voltaic circuit being also formed in this case. Thus when a zinc plate is wetted with dilute sulphuric acid, and mercury poured upon it, the zinc is immediately amalgamated.

Several amalgams are used in the arts. Tin amalgam is used for 'silvering' mirrors; amalgams of gold and silver in the processes of gilding and silvering by heat; cadmium-amalgams, copper-amalgams, and an amalgam of tin, gold, and silver, are used for stopping teeth; an amalgam of zinc and tin, sometimes with addition of bismuth, is used for coating the rubbers of electrical machines.

Aluminium-amalgam?—Klauer (Ann. Ch. Pharm. x. 391) found that potassium-amalgam laid on a lump of alum, decomposed it, the mercury taking up a considerable quantity of aluminium. Böttger (J. pr. Chem. i. 305) was not able to obtain an amalgam of aluminium in this manner; and according to Deville, metallic aluminium is not susceptible of amalgamation.

According to Cailletet (Compt. rend. xliv. 1250), aluminium (also iron and platinum) may be superficially amalgamated by contact with ammonium, or sodium-amalgam and water; also when it is immersed in acidulated water in contact with metallic mercury forming the negative pole of a voltaic battery.

Ammonium-amalgam. See i. 188.

Antimony-amalgam is said to be formed by triturating 3 pts. of heated mercury in contact with 1 part of fused antimony; or by triturating 2 pts. of antimony in a mortar with a small quantity of hydrochloric acid, and gradually dropping in 1 pt. of mercury. It is soft, and is decomposed by contact with air or water, the antimony separating in the form of a black powder.

Arsenic-amalgam.—Bergmann states that a compound containing 5 pts. mercury to 1 pt. arsenic is produced by heating and triturating the two metals together.

Barium-amalgam may be prepared by the galvanic method, or better, perhaps, by decomposing a saturated solution of chloride of barium with sodium-amalgam. It is a soft pasty mass, in which a few sandy grains may be felt. It is rapidly decomposed by water, and must therefore be kept under rock-oil.

Bismuth-amalgam.—Mercury amalgamates bismuth even at ordinary temperatures; but the amalgam is more quickly formed by pouring 2 pts. of hot mercury into 1 pt. of melted bismuth. The amalgam, which is soft at first, gradually becomes crystallo-granular. Sodium-amalgam in contact with moist neutral nitrate of bismuth, or immersed in a solution of that salt, forms a compact amalgam, with evolution of hydrogen, and separation of black pulverulent bismuth (Böttger). A small quantity of bismuth takes away but little of the fluidity of mercury, and is therefore used for adulterating that metal; according to Lucas, however (N. Trommsd. i. 195), mercury adulterated with only $\frac{1}{5000}$ pt. of bismuth forms a black powder when agitated in the air. 1 pt. of bismuth dissolved even in 1,200,000 pts. of mercury may be detected by the addition of potassium-amalgam and water, the bismuth being then raised by the galvanic action in the form of a black powder, and attaching itself to the sides of the vessel. (Serullas, Ann. Ch. Phys. [3] xxxiv. 192.)

Cadmium-amalgam.—Mercury combines readily with cadmium, even at ordinary temperatures, forming a silver-white granular amalgam, consisting of octahedral crystals; hard, brittle, heavier than mercury, and melting at 75°. When the mercury is completely saturated with cadmium, the amalgam contains 78·26 pts. mercury to 21·74 pts. cadmium, agreeing with the formula Hg^2Cd (Stromeyer). Sodium-amalgam introduced into a solution of cadmium is converted into cadmium-amalgam. (Böttger.)

Calcium-amalgam.—Produced by the action of a powerful voltaic battery on hydrate of calcium in contact with mercury; also, according to Klauer, by the action of sodium-amalgam on calcium-salts.

Cobalt-amalgam is not easily prepared by the action of sodium-amalgam on cobalt-solutions, inasmuch as a considerable quantity of cobalt-oxide is thereby precipitated. Damour immerses an amalgam of 5 pts. mercury, and 1 pt. zinc in an acid solution of cobalt-chloride supersaturated with ammonia; pours the liquid off after a few days, and decomposes it with fresh portions of zinc-amalgam as long as any gas is thereby evolved; and lastly, removes the excess of zinc by dilute sulphuric acid. The cobalt-amalgam thus obtained is silver-white, soft and dull; is attracted by the magnet even when it contains zinc (?), and becomes covered with black, pulverulent oxidised cobalt when exposed to the air.

Copper-amalgam may be formed: 1. By immersing a piece of copper-foil in a solution of nitrate of mercury.—2. By triturating mercury with common salt and verdigris.—3. By triturating 2 pts. of mercury, 2½ of verdigris, and 1 of common salt with a small quantity of heated vinegar, which must be renewed as it evaporates, and purifying the amalgam by washing.—4. By mixing 1 pt. of finely-divided copper—obtained by reducing the oxide with hydrogen, or by precipitation from the sulphate by zinc or iron—with a few drops of mercurous nitrate, and then triturating with 3 pts. of mercury, a light red amalgam is formed (Berzelius).—5. Mercury placed in contact with the negative pole of a voltaic battery, and covered with solution of cupric sulphate into which the positive wire dips, becomes perfectly saturated with copper (Grove, Phil. Mag. [3] xv. 83). According to Joule (Chem. Gaz. 1850, p. 339), the amalgam thus obtained has the composition $CuHg$; and the same definite compound is obtained by dissolving copper in mercury, and removing the excess of the latter by strong pressure (Chem. Gaz. 1850, p. 339). When, however, the pressure is very strong, or is continued for a long time, the resulting amalgam contains more than 1 at. Cu to 1 at. Hg (Joule, Chem. Soc. J. xvi. 382).—6. Copper amalgam may also be formed by treating a solution of cupric sulphate with sodium-amalgam (Klauer), or zinc-amalgam (Damour). Sodium-amalgam immersed in a mixture of cupric sulphate and sal-ammoniac forms a reddish or golden-yellow amalgam of copper and ammonium, which soon decomposes. —7. A copper-amalgam used by the Parisian dentists for stopping teeth is prepared by triturating mercurous sulphate (obtained by heating together 10 grms. of mercury and 10 grms. of strong sulphuric acid) and finely-divided copper (obtained by precipitating a solution of 23·5 grms. cupric sulphate in 10 or 12 times its weight of water, with metallic iron). The materials are triturated together under hot water for 20 or 30 minutes; the water then poured off, and the trituration repeated with fresh quantities of water as long as the water exhibits any blue colour. The amalgam is then dried, again triturated, then well kneaded, and formed into small cakes, which become quite hard in 36 to 48 hours. The amalgam thus produced contains 3 pts. copper to 7 pts. mercury. An easier mode of preparing it is to moisten the precipitated copper with solution of mercurous nitrate, then pour hot water upon it, and incorporate the required quantity of mercury by trituration; the mass, which is brittle at first, gradually softens under the pressure of the pestle.

This amalgam, which becomes quite hard by keeping, is distinguished by the property of softening and acquiring the consistence and elasticity of clay by continued pounding or kneading, and recovering its hard crystalline character when left to itself for a few hours; it may then be pulverised, exhibits a granulo-crystalline fracture, and is hard enough to engrave upon tin. When heated it swells up, and small globules of mercury show themselves on its surface, sinking into the mass again on cooling. On triturating the warmed lumps in a mortar, the amalgam is again obtained in the form of a highly plastic almost unctuous mass. Its density is the same in the soft as in the hard state, so that it does not expand or contract in hardening, and therefore fills cavities air-tight when hard, into which it has been pressed in the soft state. It is on account of this property that the amalgam is used for stopping teeth; but the copper which it contains renders it decidedly objectionable for that purpose. It may, however, be advantageously used for sealing bottles, glass tubes, &c., in cases where other plastic substances, cork, &c., cannot be used.

Iridium-amalgam is obtained as a semi-fluid mass by decomposing a concentrated solution of sodio-iridic chloride with sodium-amalgam.

Gold-amalgam.—See GOLD, ALLOYS OF (ii. 927).

Iron-amalgam.—Mercury and iron do not unite readily. A viscid amalgam is, however, obtained by immersing sodium-amalgam containing 1 per cent. sodium in a clear saturated solution of ferrous sulphate. In small globules it is attracted by the magnet, and when slowly heated on a watch-glass, exhibits the vivid sparkling of burning iron (Böttger). According to Aikin, iron-amalgam is formed by the action of zinc-amalgam on ferrous chloride; but according to Damour it cannot be produced in this way. Joule (Chem. Gaz. 1859, p. 339; Chem. Soc. J. xvi. 378) has obtained amalgams of iron by the electrolysis of a solution of ferrous sulphate, the negative pole being formed of mercury. The following table exhibits the composition and physical character of the compounds thus produced.

No.	Composition.		Specific gravity.	Remarks.
	Mercury.	Iron.		
1.	100	0·143	. .	Perfectly fluid.
2.	„	1·39	. .	Fluid.
3.	„	2·97	. .	Semi-fluid.
4.	„	11·8	12·19	Soft.
5.	„	18·3	. .	Solid: colour, greyish-white.
6.	„	47·5	. .	Solid: good metallic lustre.
7.	„	127·6	10·11	Solid: friable.
8.	„	14·74	. .	The superfluous mercury pressed out from the semi-fluid amalgam by hand.
9.	„	79	. .	Compressed rapidly, and with a force of fifty tons on the square inch.
10.	„	103·2	. .	Ditto.

Lead-amalgam.—See Lead, Alloys of (p. 534).

Magnesium-amalgam.—Magnesium combines with mercury only when heated, and forms a solid amalgam, even with large quantities of the latter (Bussy).—2. The amalgam may also be obtained by electrolysis.—3. By covering potassium or sodium-amalgam with solution of sulphate of magnesium (Klauer, Ann. Ch. Pharm. x. 89).—The amalgam thus obtained oxidises slowly in pure water, quickly in acidulated water. (H. Davy.)

Manganese-amalgam is obtained by the action of sodium-amalgam on a strong solution of manganous chloride. It is viscid, with rough blackish surface, and when heated in contact with the air, gives off mercury, tarnishes, is converted into a stiff paste, and finally leaves brown manganoso-manganic oxide.

Nickel-amalgam is obtained like cobalt-amalgam. It is solid; is attracted by the magnet; decomposes when exposed to the air, the nickel gradually oxidising till nothing but mercury is left; may be mixed with a larger quantity of mercury; gives up its nickel to hydrochloric and dilute sulphuric acid.

Osmium-amalgam is formed, according to Tennant, by decomposing aqueous osmic acid with metallic mercury; it is more or less fluid, according to the proportion of mercury contained in it.

Palladium-amalgam is formed by agitating the solution of a palladium-salt with excess of mercury. The amalgam containing Pd^2Hg is a grey powder, which, according to Berzelius, does not give off its mercury below a white heat.

Platinum-amalgam.—Platinum in the compact state does not take up mercury, but spongy platinum unites with it when the two are triturated together, in a warm mortar, or in contact with a small quantity of acetic acid. The amalgam of platinum is easily formed by immersing sodium-amalgam containing 1 per cent. sodium in a concentrated solution of platinic chloride; sodium-amalgam also converts chloroplatinate of ammonium into platinum-amalgam, with evolution of ammonia and hydrogen. The amalgam is silvery, and does not give off mercury below a bright red heat.

Joule (Chem. Soc. J. xvi. 384), by electric deposition of platinum on mercury, has obtained amalgams exhibiting the following composition and characters:

Mercury.	Platinum.	Specific gravity.	Characters.
100	15·48	14·29	Metallic lustre where rubbed.
„	21·6	. .	Solid. Dark grey.
„	34·76	14·69	Dark grey; no metallic lustre.

An amalgam of 12 platinum to 100 mercury has a bright metallic lustre, and is soft and greasy to the touch. Pressed with a force of 12 tons to the square inch, it leaves a hard button of dark grey amalgam containing 43·2 pts. platinum to 100 mercury. Joule infers from these results that the solid amalgam of platinum containing the largest quantity of mercury has the composition $PtHg^3$. A thick pasty amalgam of platinum may be obtained by exposing mercury for some time to the action of platinic chloride.

Potassium-amalgam.—1. The two metals unite even at ordinary temperatures, the combination being attended with great evolution of heat (H. Davy). 2. When mercury is placed in a cup connected with the negative pole of a voltaic battery of at least 20 pairs, and covered with a strong solution of potash in which a piece of hydrate of potassium is immersed, and into which the positive wire dips, the mercury takes up potassium (Berzelius). 1 pt. of potassium forms with 30 pts. of mercury an amalgam which, after cooling, is tolerably hard and brittle; with 70 pts. mercury it likewise forms an amalgam which is solid at ordinary temperatures, but with more than 70 pts. it forms a liquid amalgam (H. Davy). According to Gay-Lussac and Thénard, the amalgam is solid and crystalline when it contains from 70 to 96 pts. of mercury to 1 pt. of potassium, but liquid when the proportion of mercury amounts to 140. According to Böttger (J. pr. Chem. i. 303), the amalgam is perfectly solid when it contains 100 pts. of mercury to 1 pt. of potassium; with 140 mercury, it is very hard; with 180 mercury, friable and partly crystallised; with 200 mercury, viscid. The amalgam crystallises in cubes (Berzelius and Pontin). The solid amalgam fuses when slightly heated. It gives off its mercury below a red heat (H. Davy). When exposed to the air or immersed in water, it is resolved into mercury and aqueous potash, hydrogen gas being slowly evolved; a similar change is produced by aqueous acids. In contact with moist ammoniacal salts, it is resolved into a potassium-salt and ammoniacal amalgam. It easily gives up its mercury to iron and platinum. (H. Davy.)

Silver-amalgam.—A native compound of mercury and of silver, called 'amalgam' by mineralogists, and having the composition $AgHg^2$ or $AgHg^3$, is found crystallised in octahedrons, rhombic dodecahedrons, and other forms of the regular system, with dodecahedral cleavage in traces; also massive. Hardness = 3 to 3·5. Specific gravity = 10·5 to 14. Colour and streak silver-white; opaque; fracture conchoïdal; brittle, and gives a grating sound when cut with a knife. Klaproth found in amalgam from Moschellandsberg in the Palatinate, 36 per cent. silver and 64 mercury, agreeing with the formula $AgHg^2$. Heyer, on the other hand, found in amalgam from the same locality, only 25 per cent. silver, agreeing with $AgHg^3$; and a specimen from Allemont in Dauphiné, analysed by Cordier, exhibited nearly the same composition, viz. 27·5 per cent. silver. Amalgam also occurs at Rosenau in Hungary, Sala in Sweden, Almaden in Spain, and in Chile. A native silver-amalgam called *Arquerite*, occurring in crystals at Arqueros Chile, contains, according to Domeyko, 13·5 per cent. silver, and 86·5 mercury, giving the formula $AgHg^6$.

Mercury is taken up by silver slowly at ordinary temperatures, but quickly when the metal, in the form of a thin lamina, or in powder, is introduced at a red heat into heated mercury. Metallic mercury immersed in a solution of silver-nitrate, precipitates the silver in the form of a crystalline amalgam, called a silver tree, or *Arbor Dianæ*. The silver-solution should be somewhat acid, and not too much concentrated. A soft silver-amalgam is formed by the action of sodium-amalgam on a strong solution of silver-nitrate.

Artificial silver-amalgam varies in character, according to its composition and the circumstances of its formation, being sometimes a soft, or crystalline, or granular mass; sometimes consisting of ramifications of prismatic crystals placed end to end. Joule finds that the amalgam most readily formed by the action of mercury on nitrate of silver has, on the average, the composition AgHg. When the action is assisted by making the mercury the negative pole of a voltaic battery, amalgams richer in silver are obtained. The mean composition of the amalgam, after being subjected to a pressure of 72 tons on the square inch, was 43·71 silver to 100 mercury. The combination of mercury and silver is attended with a considerable contraction of volume.

Sodium-amalgam.—Sodium combines rapidly with mercury at ordinary temperatures, the combination being attended with a hissing noise and vivid combustion (Gay-Lussac and Thénard, *Recherches*, i. 246). A piece of sodium forcibly thrown upon mercury, is thrown out of the vessel with explosion, in consequence of the great heat produced (Serullas, Ann. Ch. Phys. [2] xl. 328). To form the amalgam, the two metals should be triturated together in a dry mortar fitted with a cover, and the mixture immersed in rock-oil as soon as the combustion is over (Böttger). The amalgam has the colour of mercury. When it contains 30 pts. of mercury to 1 pt. of sodium, it is tolerably hard under the file, which wears it away in the form of powder; it exhibits a crystalline, laminar fracture. When it contains 40 pts. of mercury, it is still solid, but softer than with 30 pts. (Lampadius). An amalgam containing 60 pts. of mercury to 1 pt. of sodium forms a stiff paste at 21° (Böttger). 64 pts. of mercury and 1 of sodium form a compound which exhibits a confused crystalline structure (Gay-Lussac and Thénard). 80 pts. mercury to 1 sodium: pasty at 21° (Böttger). 86 mercury to 1 sodium: a mass containing numerous small granular crystals (Gay-Lussac and Thénard). 100 mercury to one sodium: viscid, and consisting of a solid and a liquid portion (Böttger). 128 mercury to 1 sodium: liquid (Gay-Lussac and Thénard). Sodium-amalgam exhibits the same reactions as potassium-amalgam. It likewise amalgamates iron and platinum (H. Davy). It decomposes the salts of barium and strontium, and many heavy metallic salts, when a small quantity of water is present, the product being a compound of mercury with the heavy metal (Böttger, J. pr. Chem. iii. 283). It is now much used as a reducing or hydrogenating agent for effecting the substitution of hydrogen for chlorine, bromine, &c., in organic compounds.

Amalgam of Potassium and Sodium.—5 pts. potassium and ½ pt. sodium melted together by heating them under rock-oil, form an alloy which is fluid like mercury at 9°, but when brought in contact with 100 pts. of mercury, unites therewith into a very solid mass. (Böttger.)

Strontium-amalgam.—Prepared like that of barium, which it resembles, but decomposes more quickly under a mixture of the solutions of chloride of strontium and chloride of calcium, as well as under water. When exposed to the air for eight or ten hours, it is converted into carbonate of strontium, with separation of mercury.

Tellurium-amalgam.—Mercury and tellurium are said to unite directly, forming a tin-coloured amalgam.

Thallium-amalgam.—The two metals unite readily, forming a crystalline amalgam. (Crookes.)

Tin-amalgam.—Mercury and tin unite quickly, even at ordinary temperatures, still more quickly on pouring mercury into melted tin. A piece of tin, the lower end of which is immersed for four weeks in mercury, is penetrated through and through by the mercury, and exhibits cracks; its lower end becomes attenuated by solution of the metal, and the immersed part is found to be covered with six-sided tables, some of which float about in the mercury. If a square bar of tin, whether cast in a square form, or hammered or filed square from a round bar, be kept for a few days under mercury, it splits in directions proceeding from the lateral edges to the opposite diagonals, thereby dividing itself into four triangular prisms, easily separated by a knife; at the same time, a four-sided pyramid is formed at each end of the square bar. If the piece of tin has any other form, cracks are produced in other directions (Daniell, J. of Roy. Inst. i. 1). Sodium-amalgam immersed in a concentrated solution of stannous chloride, yields a viscid amalgam of tin. (Böttger.)

Tin-amalgam has a tin-white colour; and if the mercury is not in too great excess, is brittle, granular, and according to Daubenton, crystallises in cubes.

$SnHg$ and $SnHg^2$ do not fuse till heated above 100°. (Regnault.)

Sn^3Hg^2 has at 26° a specific gravity of 8·8218; $SnHg$, 9·3185; $SnHg^2$, 10·3447; $SnHg^4$, 11·3816. 1 vol. of tin with 1 vol. of mercury forms an alloy whose specific gravity at 27° is 10·4729; 1 vol. tin with 2 vol. mercury, 11·4646; and 1 vol. tin with 3 vol. mercury, 12·0257. In most cases, therefore, condensation takes place; in the single instance of 1 vol. tin to 2 vol. mercury, however, this condensation is scarcely perceptible. (Kupffer, Ann. Ch. Phys. [2] xl. 293.)

The compound obtained by fusing 4 pts. of tin with 1 pt. of mercury, yields, if pulverised after cooling, a kind of mosaic silver, which, when rubbed on the polishing-stone, acquires the metallic lustre. The *silvering* of mirrors is likewise an amalgam of tin.

Joule obtained beautiful crystalline amalgams by making mercury negative in a solution of stannous chloride. The amalgam containing 100 mercury to 51 pts. tin, had a specific gravity of 10·518; that containing 100 mercury to 44·1 tin, a specific gravity of 10·94: hence the combination is attended with contraction of volumes. The amalgam of tin is decomposed by pressure, the mercury left after long-continued high pressure having a volume little more than one-eighth of the entire mass.

An amalgam of *tin* and *bismuth* is obtained by melting together 2 pts. of tin, 2 pts. of bismuth, and 1 pt. of mercury.

An amalgam of 2 pts. *tin* and 1 pt. *cadmium* is used for stopping teeth. The two metals are melted in an iron ladle, slightly warmed; mercury is added; the whole is poured into an iron mortar, and rubbed with a wooden pestle, till it acquires a soft buttery consistence; and the excess of mercury is squeezed out through leather. The residue is almost granular, but becomes soft and plastic when kneaded by the hand.

An amalgam of *tin* and *lead* may be formed by introducing an alloy of the two metals into mercury.

Amalgams containing *tin*, *lead* and *bismuth* are described under LEAD (p. 537). An amalgam of 8 pts. bismuth, 5 lead, 3 tin, and 7 or 8 mercury is recommended by Brame for coating the rubbers of electrical machines.

An amalgam of *tin, silver* and *gold* is also used as a cement for the teeth. It is prepared by melting together 1 pt. gold and 3 pts. silver, adding 2 pts. tin to the melted mass, pulverising the resulting alloy, and kneading it together with an equal weight of mercury.

Zinc-amalgam.—When zinc-filings are triturated with mercury, at ordinary temperatures, combination takes place slowly; at a higher temperature, still somewhat under the boiling point of mercury, the metals combine easily, and still more readily when mercury is mixed with melted zinc. A bar of zinc, immersed to half its length in mercury for ten days, becomes pointed at bottom, and covered, especially on the upper part of the immersed end, with six-sided tables of the amalgam (Daniell). When zinc is placed in contact with mercury and a dilute acid, a galvanic action is set up (ii. 420), and the zinc becomes covered with mercury, which then penetrates into the interior, and converts the whole of the metal into an amalgam. As soon as the zinc is completely covered with mercury, the evolution of hydrogen ceases; but it begins again on bringing the amalgam in contact with iron, copper, or platinum, to which metals the mercury is then transferred (Döbereiner). Sodium-amalgam immersed in a concentrated solution of sulphate of zinc, forms a viscid amalgam of zinc. (Böttger.)

The amalgam is usually prepared by cooling melted zinc to as low a temperature as it will bear without solidifying, and then pouring in the mercury in a fine stream, keeping the liquid constantly stirred. If this precaution be neglected, part of the mercury is converted into vapour, sometimes throwing the melted metal about.

8 pts. zinc to 1 pt. mercury: very brittle.

1 pt. zinc and 4 or 5 pts. mercury form an amalgam sometimes used for coating the rubbers of electric machines; it is brittle and pulverulent.

1 pt. zinc to 6 pts. mercury: tin-white, granular, brittle; melts at the boiling point of olive-oil, but does not give off mercury till raised to a higher temperature. At a dull red heat, it decrepitates strongly; at a stronger red heat, it burns with great brilliancy. It is permanent in dry air. Cold dilute nitric acid decomposes it readily, and leaves the mercury unaltered till all the zinc is dissolved. Dilute sulphuric and hydrochloric acid act on it but slowly. Ammonia and sal-ammoniac also dissolve out the zinc very slowly, and form water. Zinc-amalgam immersed in the solution of a neutral salt of chromium, uranium, manganese, or iron, merely throws down the oxide; but from neutral solutions of cobalt, nickel, and copper, it precipitates the metal, which then combines with the mercury. (Damour, Ann. Min. [3] xv. 41; also J. pr. Chem. xvii. 345.)

From an amalgam richer in mercury, six-sided laminæ containing 2 pts. zinc and 5 mercury, separate out on cooling. The portion which remains liquid is a solution of zinc in excess of mercury. 1 pt. of zinc dissolved in 8,000 pts. of mercury may be detected by the black powder which forms on the surface when the mercury is agitated in contact with the air.

Zinc-amalgam immersed in caustic potash liberates pure hydrogen. When zinc-amalgam is immersed in aqueous ferrous chloride, and a crystal of a nitrate is placed upon it, a black spot is gradually formed on the surface of the amalgam, consisting of reduced iron, which is immediately taken up by the mercury. The presence of a nitrate is essential to the production of this effect; chlorates and other salts do not produce it. (Runge, Pogg. Ann. ix. 479.)

Joule, by the electrolytic method, has obtained amalgams of zinc having the following composition and properties:

Mercury.	Zinc.	Specific gravity.	
100	39·4	11·34	White and crystalline.
„	122·8	8·935	„
„	134·9	8·349	Prepared from hot sulphate of zinc.

The specific gravity of the first of these amalgams indicates a certain contraction of volume. Pressure appears to decompose it, mercury being expelled till the amalgam consists of about 1 at. Hg to 3 at. Zn.

Amalgams of *tin* and *zinc* are used for coating the rubbers of electrical machines. Kienmayer recommends as the best proportion; 1 pt. zinc, 1 pt. tin, and 2 pts. mercury, Singer recommends 2 pts. zinc, 1 pt. tin, and 3½ to 6 pts. mercury.

MERCURY, ANTIMONIDE OF. See page 886.

MERCURY, ARSENIDE OF. See page 886.

MERCURY, BROMIDES OF. Mercury forms two bromides, distinguished as *mercurous* and *mercuric*.

α. **Mercurous Bromide.** Hg^2Br or HhgBr.—This compound is formed: 1. By subliming an intimate mixture of 1 at. mercury and 1 at. mercuric bromide (Löwig).—2. By precipitating mercurous nitrate with aqueous bromide of potassium (Balard). When prepared by the first process, it forms a fibrous mass (Löwig); long needles which are yellow while hot, but become whitish on cooling (O. Henry, J. Pharm. xv. 56). By (2): white powder (Balard); yellowish-white flakes (O. Henry). Specific gravity 7·307 (Karsten). It is tasteless and inodorous; fusible, and volatilises undecomposed at a low red heat.

When heated with *phosphorus*, it is resolved into bromide of phosphorus and phosphide of mercury (Löwig). Treated with cold aqueous *ammonia*, and then washed with water containing ammonia, it leaves a grey powder, which contains globules of mercury, and when heated, gives off ammonia, and yields a sublimate of mercury, mercurous bromide, and mercuric bromide (Rammelsberg). With caustic *potash*, it yields mercurous oxide and bromide of potassium. When boiled with aqueous *bromide* or *chloride of ammonium*, it yields a solution of mercuric bromide, with a residue of metallic mercury (Löwig). It is not perceptibly soluble in cold *carbonate*, *chloride*, or *succinate of ammonium*, while the same liquids, when hot, dissolve it with tolerable facility, leaving, however, a grey-pulverulent residue [metallic mercury]; it is not perceptibly soluble in *sulphate* or *nitrate of ammonium*, even at the boiling heat. (Wittstein.)

β. **Mercuric Bromide.** HgBr or $Hhg''Br^2$.—1. Mercury unites with bromine at ordinary temperatures, forming this compound, the combination being attended with evolution of heat, but not of light (Balard).—2. The same compound is formed by agitating mercury with water, adding bromine as long as its colour is destroyed, then boiling, filtering, and leaving the solution to crystallise.—3. By dissolving mercuric oxide in hot aqueous hydrobromic acid, and leaving the solution to crystallise.—4. By subliming mercuric sulphate with bromide of potassium (Löwig). The sublimate contains also mercurous bromide (O. Henry).—5. By mixing aqueous mercuric nitrate with bromide of potassium, evaporating as long as bromide of mercury crystallises out, and purifying the product by solution in alcohol. The mother-liquid evaporated to dryness leaves a residue, from which boiling alcohol still extracts a small quantity of the compound. (Löwig.)

Mercuric bromide crystallises from the aqueous solution in soft, silvery laminæ; from the alcoholic solution in white needles (Löwig.) According to Handl (Jahresb. 1859, p. 226), the crystals are rhombic prisms, $\infty P \,.\, oP$, cleavable parallel to oP, and having the angles $\infty P : \infty P = 68° 24'$ and 111° 26′. They are isomorphous with sublimed mercuric chloride. The product obtained by (5) has, after drying at a strong heat, a specific gravity of 5·9202 (Karsten). Mercuric bromide melts and sublimes when heated. It dissolves in 94 pts. *water* at 9° (Lassaigne) and in 4 pts. of boiling water, the greater part separating as the liquids cool. The aqueous solution reddens litmus. It dissolves very easily in *alcohol*, still more in *ether*.

With *phosphorus* it forms bromide of phosphorus. Heated with *antimony* or *arsenic*, it gives up its bromine. Its aqueous solution exposed to *sun-light*, or placed in contact with *mercury* or *copper*, or mixed with *cuprous bromide* dissolved in hydrobromic acid, deposits mercurous bromide. With a small quantity of *sulphydric acid* it yields a white, and with a larger quantity a black precipitate (H. Rose). With *ammonia* it forms a white, with fixed alkalis a yellow precipitate (Löwig). *Hypochlorite of sodium* added to the solution throws down mercuric oxychloride (Rammelsberg), and hypochlorous acid converts mercuric bromide into mercuric chloride and bromate, the action being attended with evolution of chlorine and bromine (Balard). Heated with *nitric* or *sulphuric acid*, it gives off vapour of bromine (Balard); but according to H. Rose (Analyt. Chem.) it is not decomposed by sulphuric acid.

Double Salts of Mercuric Bromide.—Mercuric bromide unites with the more basic metallic bromides, forming easily soluble double salts (called by Bonsdorff, bromohydrargyrates), losing thereby its power of reddening litmus. Those containing the bromides of the alkali-metals are crystallisable.

Ammonium-salt.—Mercuric bromide dissolves abundantly in aqueous bromide of ammonium. Alkaline carbonates added to the solution throw down bromide of dimercurammonium. (Löwig.)

The *barium-salt* crystallises in highly lustrous prisms, which deliquesce in moist air. (Bonsdorff.)

Calcium-salt.—A solution of bromide of calcium saturated with mercuric bromide yields by spontaneous evaporations, at first tetrahedrons and octahedrons, which have a strong lustre, are permanent in the air, and are decomposed by a small quantity of water, but dissolve completely when heated and crystallise out again on cooling. If the evaporation be carried further, prisms or needles are obtained, which deliquesce even in dry air. (Bonsdorff.)

The *iron-salt* [? ferric or ferrous] forms yellowish very deliquescent prisms. (Bonsdorff.)

Magnesium-salts.—A solution of mercuric bromide and bromide of magnesium yields, by evaporation over oil of vitriol, first broad thin laminæ, permanent in the air and probably containing $MgHg^2Br^3$?, then very deliquescent crystals containing $MgHgBr^2$. (Bonsdorff.)

The *manganese-salt* crystallises in light red very hygroscopic prisms.

Potassium-salts.—A solution of the salt KHg^2Br^3 or $KBr.2HgBr$ is obtained by saturating a cold moderately concentrated solution of bromide of potassium with mercuric bromide, in anhydrous yellow octahedrons (Löwig), in flat rhombic prisms permanent in the air and containing 1 at. water. The crystals melt when heated, and yield a sublimate of mercuric bromide (Löwig). A solution of equal parts of this salt and bromide of potassium yields the salt K^2HgBr^3 (?) in prisms which are permanent in the air. (Bonsdorff.)

The *sodium-salt* crystallises partly in needles, partly in rhombic prisms, and deliquesces in moist air.

Strontium-salts.—*α.* $SrHgBr^2$ or $SrBr.HgBr$ forms crystals soluble in water in all proportions.—*β.* $SrHg^2Br^3$ or $SrBr.2HgBr$. A solution of 1 at. bromide of strontium in twice its weight of water, takes up at 50°, 3 at. mercuric bromide, and the solution on cooling deposits 1 at. mercuric bromide and then yields small crystals of the salt *β*. (Löwig.)

The *zinc-salt* crystallises in prisms and tables deliquescent in moist air. (Bonsdorff.)

MERCURY, CHLORIDES OF. Mercury forms two chlorides, analogous to the bromides.

Mercurous Chloride. Hg^2Cl or $HhgCl$.—*Hemichloride, Dichloride, Subchloride, Protochloride, Submuriate of mercury; Calomel; salzsaures Quecksilberoxydul, versüsster Sublimat, versüsstes Quecksilber, Kalomel; Chloretum hydrargyri, Hydrargyrum muriaticum mite, Mercurius dulcis,* s. *kalomelanicus,* s. *loticus, Draco mitigatus, Aquila mitigata,* s. *alba,* s. *cœlestis,* s. *Mercurii, Panacea mercurialis,* s. *cœlestis,* s. *Mercurii; Protochlorure de mercure.*

This compound is found native, as *horn-quicksilver*, in dimetric crystals exhibiting the combination P . ∞P∞, like figure 227 (ii. 135), also with ∞P, P∞ and oP. Length of principal axis = 1·744; P : P in the terminal edges = 98° 7′; in the lateral edges = 135° 56′. It occurs also in crystalline coats and granular. Hardness = 1 to 2. Specific gravity = 6·482. It has a dirty white colour and adamantine lustre, yellow when scratched; translucent in thin splinters. Sectile. Fracture conchoïdal. It is found, with cinnabar, at Moschellandsberg in the Palatinate, also at the quicksilver mines of Idria and Almaden, and at Horzowitz in Bohemia.

Mercurous chloride is produced: 1. By the direct combination of mercury and chlorine, slowly at ordinary temperatures, more quickly at the boiling heat of mercury, the combination being then attended with a yellowish red flame, and mercuric chloride being likewise formed.—2. By heating mercuric chloride with metallic mercury. 3. By the action of sulphurous acid and other reducing agents on mercuric chloride. 4. By agitating mercury with a solution of ferric chloride, the action being accelerated by the presence of free hydrochloric acid.—5. By the action of hydrochloric acid on mercurous oxide, or by precipitating a mercurous salt with a soluble chloride.

Preparation.—Mercurous chloride in the pulverulent form, called calomel, is extensively used in medicine. It may be prepared either in the dry or in the wet way.

a. In the dry way.—1. By triturating 4 pts. (1 at.) of mercuric chloride with 3 pts. (1 at.) of mercury, the mixture being moistened with water or alcohol, and the trituration continued till the mercury has lost its fluidity—then gradually heating the mixture in a glass flask or retort till it sublimes. A large portion of the mercuric chloride is converted into calomel during the trituration. Trautwein heats the deadened mixture, gently at first, for a few hours, and pulverises it once more before sublimation. 2. By subliming an intimate mixture of equal parts of mercurous sulphate and common salt:

$$Hhg^2SO^4 + 2NaCl = Na^2SO^4 + 2HhgCl.$$

Planche (Ann. Chim. lxvi. 168) triturates 8 pts. of mercury, 18 pts. of dry monobasic mercuric sulphate, and 6 pts. of water, till the fluidity of the metal is destroyed, and heats the resulting mercurous sulphate with an equal weight of common salt, till a sublimate is obtained.—3. By deadening 2 at. mercury with 2 at. common salt and 1 at. peroxide of manganese, and heating the mixture to sublimation with 2 at. sulphuric acid:

$$\mathrm{Hhg^2 + 2NaCl + MmnO^2 + 2H^2SO^4 = 2HhgCl + Na^2SO^4 + MmnSO^4 + 2H^2O.}$$

4. By triturating mercury with common salt, ferric sulphate, and a small quantity of water, till the metal has lost its fluidity, and subjecting the mixture to sublimation. (Schaffhäutl, Ann. Ch. Pharm. xliii. 25). The basic ferric sulphate, often occurring as a waste product, may be made available for this process; a small quantity of ferric chloride may sublime together with the calomel (Schaffhäutl). The reaction is probably:

$$\mathrm{Ffe^2(SO^4)^3 + 6NaCl + Hhg^2 = 3(Na^2SO^4) + 2FfeCl^2 + 2HhgCl.}$$

The calomel set free in the form of vapour by either of these processes (1—4), is either allowed to collect in the form of a dense, fibrous sublimate, and the product carefully pulverised; or the calomel vapour is cooled under such circumstances that it solidifies in the form of a soft powder instead of a solid cake. This object is attained, according to Jewel and O. Henry (J. Pharm. viii. 545), by causing the calomel vapour to pass into a chamber into which vapour of water is injected on the other side. According to the process now adopted in this country, on the other hand, the calomel, or the ingredients from which it is prepared, is heated in a cast-iron cylinder 2½ feet long and 1 foot wide, one end of which is provided with an opening serving to introduce and remove the materials, and closed during the operation, while the other end terminates in a contracted neck which opens into the upper part of a brick chamber, 4 feet long and broad, and 6 feet high. In this chamber the calomel condenses in the form of a soft powder. As the iron of the tube decomposes a portion of the calomel, a small quantity of mercuric chloride is added to the mixture (Calvert, J. Pharm. [3] iii. 121). Soubeiran (J. Pharm. xxix. 502) adopts the same process, excepting that he heats the materials in an earthen retort, and uses a large earthen vessel as a condensing chamber. The pulverulent calomel obtained by either of these processes is washed with a large quantity of warm water, or a small quantity of warm alcohol, to free it from the corrosive sublimate with which it is usually contaminated.

6. *In the wet way.*—1. By precipitating a warm dilute solution of mercurous nitrate with excess of common salt or sal-ammoniac, and washing the precipitate thoroughly with cold water. The calomel obtained by this process, first proposed by Scheele, is in the form of a remarkably fine powder, and has consequently somewhat more active medicinal properties than the ordinary preparation. Its more energetic action may perhaps be partly due to an admixture of basic mercurous nitrate, or mercuric oxide, which, according to Buchner, Mialhe, and others, are sometimes found in it. This admixture, however, does not occur if the solution of mercurous nitrate be largely diluted, and, if necessary, filtered, before being mixed with the soluble chloride, and if the common salt or sal-ammoniac be added in excess, and the liquid heated for some time in contact with the precipitate. To the same end, Sefström, Geiger, and Trautwein (Repert. Pharm. xi. 72; xii. 155) recommend that a little nitric acid be added to the mercurous solution before mixing; and Chenevix advises the addition of hydrochloric acid to the solution of common salt. In that case, however, the liquid must not be heated so much, as, otherwise, part of the calomel will be redissolved in the form of mercuric chloride. According to Dumas, the calomel obtained by the use of common salt always contains more or less of that substance, and cannot be freed from it by washing; the presence of the salt renders the calomel thus prepared more soluble than that obtained by sublimation; but Mialhe (J. Pharm. xxii. 586) found only traces of common salt, and no difference in the solubility.—2. Sulphurous acid gas, evolved by heating sulphuric acid with charcoal, is passed into a solution of mercuric chloride saturated at 50°. The reaction is as follows:

$$\mathrm{2HhgCl^2 + SO^2 + 2H^2O = 2HhgCl + 2HCl + H^2SO^4}$$

The filtered liquid still contains a certain quantity of undecomposed mercuric chloride, and, therefore, still gives a precipitate of calomel when heated with sulphurous acid to the boiling point (Wöhler, Ann. Ch. Pharm. xc. 124). According to Sartorius (*ibid.* xcvi. 325), the decomposition is almost complete in the first instance, provided the solution is sufficiently dilute (1 pt. mercuric chloride to 80 water) and the liquid saturated with sulphurous acid is heated for some time to 70° or 80°. Calculation requires a product of 84 per cent.; experiment gave 84·6 per cent.

Impurities and Adulterations.—1. *Mercuric chloride:* Cold water or alcohol agitated with the powder for some time and then filtered, turns brown on the addition of sulphydric acid, &c. 2. *Basic mercurous* or *mercuric nitrates*: Red fumes evolved on heating the substance in a flask or tube till it sublimes. 3. *Metallic mercury:* Grey colour; globules of mercury discernible under the microscope. 4. Pounded *heavy spar* and similar impurities remain behind on sublimation. 5. *Gum* and other organic substances: Empyreumatic odour on the application of heat; solubility in water or alcohol, &c.

Properties.—Sublimed calomel crystallises in dimetric forms like the native mineral, but the prisms are generally united in fibrous masses. Specific gravity of the artificial product, 6·9920 (Karsten); 7·140 (P. Boullay). Vapour-density, according to Mitscherlich's observation, 8·35; by calculation, 8·25 $\left(= \frac{200 + 35 \cdot 5}{2} \times 0 \cdot 0693\right)$. It is dirty white, translucent, and has a very high refractive and dispersive power; it acquires a transient yellow colour when heated in the state of powder. Precipitated calomel is a white, heavy powder, with a tinge of lemon-yellow. Calomel volatilises below a red heat, without previous fusion. According to Faraday, it does not volatilise at ordinary temperatures. It is tasteless and inodorous, and may be regarded as quite insoluble in water; for, according to Pfaff, a perceptible precipitate is produced in a solution of mercurous nitrate by hydrochloric acid diluted with 250,000 pts. of water.

Decompositions.—1. Calomel becomes dark grey on exposure to light.—2. Heated in a current of *phosphorus-vapour*, it yields phosphite of mercury and trichloride of phosphorus (H. Davy). 3. When heated with a small quantity of *sulphur*, it yields cinnabar and mercuric chloride; with a larger quantity of sulphur, the products are cinnabar and chloride of sulphur:

$$2HhgCl + S = HhgCl^2 + HhgS$$

$$\text{and } HhgCl + S^2 = HhgS + SCl.$$

4. When immersed in cold aqueous *sulphurous acid*, it turns grey, and in the same liquid at the boiling heat it becomes greyish-black, from loss of chlorine. In this greyish-black powder, no metallic mercury can be discovered with the lens; but when heated, it is resolved into calomel and metallic mercury; it is probably, therefore, a subchloride (A. Vogel).—5. Calomel gives up its chlorine to many *metals*, both in the dry and in the wet way. On boiling it with *copper* and water, a green solution is quickly formed, and the copper becomes covered with a black film, from which hydrochloric acid extracts cupric oxide, leaving a residue of metallic mercury (A. Vogel, J. pr. Chem. viii. 107).—6. By aqueous *stannous chloride*, it is reduced to the metallic state, after some time at ordinary temperatures, but quickly on boiling (A. Vogel, Kastn. Arch. xxiii. 78). With *trisulphide* (*mineral kermes*) *or pentasulphide of antimony*, it is gradually converted into black sulphide of mercury and trichloride of antimony.—8. Calomel triturated with *iodine* and water, yields mercuric chloride, which dissolves, and mercuric iodide, of which the water takes up a small portion. (Planche and Soubeiran, J. Pharm. xii. 651.)

$$2HhgCl + I^2 = HhgCl^2 + HhgI^2.$$

9. Calomel digested in aqueous solutions of the *iodides of the alkali-metals*, *magnesium zinc*, or *iron*, yields dark green mercurous iodide, and an aqueous metallic chloride. The mercurous iodide thus produced remains unchanged for a long time in the dark; but when exposed to light, it first becomes yellow, and then red from loss of mercury—fuses into a black-brown liquid—gives off mercury and mercuric iodide—and leaves a white residue of metallic chloride, together with the excess of metallic iodide employed (Labouré, J. Pharm. iv. 329). 10. Hot *nitric acid* dissolves calomel, with evolution of nitric oxide gas, forming a solution of mercuric chloride and mercuric nitrate:

$$6HhgCl + 4HNO^3 = 3HhgCl^2 + 3HhgNO^3 + 2H^2O + NO.$$

Cold *sulphuric acid* neither dissolves nor decomposes calomel, even after a long time; but hot sulphuric acid dissolves it (the liquid solidifying to a white saline mass on cooling), giving off sulphurous anhydride, yielding a sublimate of mercuric chloride, and leaving a residue of mercuric chloride mixed with mercuric sulphate. (A. Vogel.)

$$2HhgCl + 2H^2SO^4 = HhgCl^2 + HhgSO^4 + SO^2 + 2H^2O.$$

11. Calomel immersed in aqueous *hydrocyanic acid* yields metallic mercury and a liquid which contains cyanide of mercury and hydrochloric acid (Scheele, Opusc. ii. 195). Part of the calomel, however, remains undecomposed, or, at least, undissolved, even when an excess of hydrocyanic acid is present; the undissolved portion is not metallic mercury, but a black powder which, when heated, gives off calomel vapour, together with a small quantity of permanent gas, and leaves a carbonaceous powder

(Soubeiran, J. Pharm. xv. 523). The decomposition by hydrocyanic acid must therefore be more complicated than that which would be expressed by the equation:

$$2HhgCl + 2HCy = Hhg + HhgCy^2 + 2HCl,$$

and deserves further examination; to the medical practitioner, it is important to know that the mild substance calomel is converted by hydrocyanic acid into a compound which acts so violently as cyanide of mercury.—12. Calomel heated with dry *fixed alkalis*, yields mercury, oxygen gas, and a chloride of the alkali-metal:

$$2HhgCl + 2KHO = 2KCl + Hhg^2 + H^2O + O.$$

By *aqueous fixed alkalis* it is converted into black mercurous oxide, a chloride of the alkali-metal remaining in solution. Calomel likewise blackens when immersed in aqueous *ammonia*, not, however, by conversion into mercurous oxide, but into chloride of mercurosammonium ($(NH^3Hhg)Cl$). The supernatant ammoniacal liquid contains a small quantity of mercury in solution. *Carbonate of ammonium* colours calomel grey and quickly dissolves it, with the exception of a small grey residue of metallic mercury. *Carbonate of magnesium* exerts no action in the cold, even in the presence of water; but at the boiling heat, carbonic anhydride is evolved, mercury separated, and a solution formed, containing mercuric oxide in combination with magnesia (Buchner, Repert. Pharm. iii. 31; iv. 289). According to A. Vogel, Jun. (Repert. Pharm. [3] i. 34), calomel heated with water and *carbonate of calcium* (or magnesium) is converted into mercurous (and mercuric ?) oxide and metallic mercury, carbonic anhydride being evolved and chloride of calcium formed. The carbonates of *barium* and *strontium* act in a similar manner, but not so strongly. When calomel is boiled with pounded *gypsum*, chloride of calcium and mercuric sulphate are formed; a similar effect is produced by boiling with *sulphate of sodium*.—13. By *aqueous vapour* and *boiling water*, calomel is partly converted into metallic mercury, or into a grey compound of calomel with excess of mercury and soluble mercuric chloride.—14. Boiling *hydrochloric acid* quickly converts calomel into mercuric chloride and metallic mercury. On the other hand, when water containing hydrochloric acid is boiled in an open vessel with calomel, the calomel is completely converted into mercuric chloride, without separation of mercury.

Chloride of potassium, *chloride of sodium*, and especially *chloride of ammonium*, convert calomel into mercuric chloride, and unite with the latter forming double salts. Hence calomel should never be prescribed for internal use in conjunction with either of these alkaline chlorides, especially sal-ammoniac. [For further details relating to this and other reactions of calomel, see *Gmelin's Handbook*, vi. 48–53.]

Compounds of Mercurous Chloride.—*a*. With *Ammonia*. 100 pts. of dry calomel absorb 7·38 pts. ammonia-gas, forming the compound NH^3HhgCl. The compound is black, but gives off ammonia on exposure to the air, and leaves white mercurous chloride (H. Rose). See MERCURY-BASES, AMMONIACAL.

β. With *Chloride of Sulphur*. $2HhgCl.SCl^2$.—Produced by intimately triturating 27 pts. mercuric chloride and 6 pts. washed and dried flowers of sulphur, and gently heating the mixture in a porcelain dish covered with a glass funnel: it then effloresces in slender crystals. These must be taken out after cooling and the operation repeated as long as any efflorescence is produced. The compound may also be prepared by mixing calomel and dichloride of sulphur to a stiff paste in a retort, and gently heating the mixture after it has stood for twenty-four hours. The excess of sulphur-chloride then distils over first; afterwards the mass gradually melts and acquires a red colour; and finally the salt sublimes in right rectangular prisms with rhombic acumination: they are yellowish white when cold, and are instantly decomposed by water. (Capitaine, J. Pharm. xxv. 525 and 566.)

γ. With *Platinous oxide*.—This compound is produced in the form of a brown powder on mixing mercurous nitrate with platinic chloride. On heating it, mercurous chloride sublimes, and platinous oxide remains behind.

δ. With *Stannous Chloride*. $2HhgCl.SnCl^2$.—Prepared by intimately mixing 1 pt. of finely pulverised tin-amalgam (3 pts. tin to 1 pt. mercury) with 24 pts. calomel, filling a retort to about one-fourth with the mixture, and exposing it to a heat gradually rising to 250°. The mass when cold is pulverised and heated in a flask to 300°, whereupon the double chloride sublimes in very small white arborescent crystals, and metallic mercury remains. The crystals are decomposed by water. (Capitaine, J. Pharm. xxv. 549.)

ε. With *Sulphuric anhydride*.—Calomel absorbs the vapour of sulphuric anhydride, forming a white translucent mass. (H. Rose, Pogg. Ann. xliv. 325.)

Mercuric Chloride. $HgCl$ or $HhgCl^2$.—*Protochloride*, *Bichloride*, *Muriate of Mercury*, *Corrosive Sublimate; aetzender Quecksilber-sublimat*, *Aetzsublimat*, *Sublimat; Deutochlorure de Mercure*, *Sublimé corrosif; Mercurius sublimatus corrosivus*, *Hydrargyrum corrosivum album*.

This compound is produced:—1. By burning mercury in excess of chlorine gas.—2. By dissolving mercury in aqua regia containing excess of hydrochloric acid, evaporating, dissolving the residue in boiling water, and leaving the salt to crystallise by cooling.—3. By dissolving mercuric oxide in hydrochloric acid, and in general by double decomposition of mercuric oxide or a mercuric salt with metallic chlorides.

It is prepared on the large scale by decomposing mercuric sulphate with chloride of sodium. An intimate mixture of equal parts of common salt and mercuric sulphate (prepared by boiling 4 pts. mercury with 5 pts. strong sulphuric acid, till the mixture is reduced to a dry saline mass) is exposed to a gradually increasing heat, in a glass flask having a long wide neck, or better in a narrow-necked retort; mercuric chloride then sublimes on the cold part of the vessel, while sulphate of sodium remains behind. On account of the extremely poisonous nature of the vapours, the process must be performed under a chimney having a good draught. The mercuric sulphate frequently contains a small quantity of mercurous sulphate, which is converted by the chloride of sodium into calomel: to prevent this contamination, a small quantity of peroxide of manganese is added to the mixture; or 10 pts. mercury, 3 common salt, 3 peroxide of manganese, 11 sulphuric acid and 3 water, are triturated together, and the mixture is then heated as above:

$$Hhg + 2NaCl + MmnO^2 + 2H^2SO^4 = HhgCl^2 + Na^2SO^4 + MmnSO^4 + 2H^2O.$$

Another very good method is to mix a boiling concentrated solution of mercurous nitrate with concentrated hydrochloric acid as long as a precipitate is formed, and boil the latter with a quantity of hydrochloric acid equal to that which was used for the precipitation. The reaction is:

$$HhgNO^3 + 2HCl = HhgCl^2 + H^2O + NO^2.$$

The solution on cooling deposits the mercuric chloride in beautiful crystals.

Mercuric chloride crystallises in two forms, both belonging to the trimetric system. The crystals which separate from the alcoholic solution exhibit the combination $\infty P . \breve{P}\infty . oP . P$. Ratio of axes $a : b : c = 0·7254 : 1 : 1·0686$. Angle $\infty P : \infty P$ in the macrodiagonal principal section = 71° 55′; $\breve{P}\infty : \breve{P}\infty$ in the basal principal section = 93° 48′.—For the crystals obtained by sublimation, $a : b : c = 0·9347 : 1 : 0·3396$. Angle $\infty P : \infty P$, in the macrodiagonal principal section = 86° 8′; $\infty\breve{P}2 : \infty\breve{P}2$ = 50° 6′; $\breve{P}\infty : \breve{P}\infty$ in the basal principal section = 37° 30′; $2\breve{P}\infty : 2\breve{P}\infty$ in the same 68° 22′. The crystals exhibit these faces together with $\infty\breve{P}\infty$. They are white, and exhibit various degrees of translucency up to complete transparency. Specific gravity = 5·4032 (Karsten); 5·420 (Boullay). Vapour-density 9·8 (Mitscherlich): by calculation, 9·48 $\left(= \frac{200 + 2 . 35·5}{2} \times 0·0693\right)$.

Mercuric chloride melts at 265°, boils at 295°, and volatilises somewhat more easily than calomel, even at ordinary temperatures. It has a disagreeable metallic taste and is a very powerful acrid poison. It dissolves in *water*, *alcohol* and *ether*. According to Poggiale, 100 pts. water at different temperatures dissolve the following quantities of mercuric chloride.

Temperature.	Quantity of salt dissolved.	Temperature.	Quantity of salt dissolved.
0°	5·73	60°	13·86
10	6·57	70	17·29
20	7·39	80	24·32
30	8·43	90	37·05
40	9·62	100	53·96
50	11·34		

In *alcohol* the salt is much more soluble, requiring only 2¼ pts. at ordinary temperatures, and 1⅙ pts. at the boiling point of alcohol; and it is almost equally soluble in *ether*. Hence when an aqueous solution of mercuric chloride is shaken up with ether, the ether extracts the greater part of it. Mercuric chloride volatilises in somewhat considerable quantity with the vapours, when its alcoholic or ethereal solution is boiled.

Mercuric chloride dissolves in considerable quantity in boiling concentrated *hydrochloric acid*, and the solution solidifies on cooling to a crystalline mass having a mother-of-pearl lustre, which, however, becomes fluid again at the heat of the hand. This mass consists, according to Boullay, of an *acid mercuric* or *hydromercuric chloride* $2HhgCl^2.HCl$. When exposed to the air, it effloresces, gives off the excess of acid, and leaves the neutral chloride. Mercuric chloride likewise dissolves with great facility in *nitric acid*, and crystallises from the solution by cooling or evaporation. *Sulphuric* acid has no action upon it.

Many metals, viz. *arsenic*, *antimony*, *bismuth*, *zinc*, *tin*, *lead*, *iron*, *nickel*, and *copper*, decompose mercuric chloride in the dry way, withdrawing the half or the whole of its chlorine, and separating calomel or metallic mercury, which latter forms an amalgam with the excess of the other metal. *Arsenic* forms trichloride of arsenic and a brown sublimate. An intimate mixture of 3 pts. *antimony* and 1 pt. corrosive sublimate, well pressed into a glass, becomes hot and liquid in the course of half an hour, and on the application of heat, yields trichloride of antimony and metallic mercury. Tin heated with mercuric chloride yields a distillate of stannic chloride, and a grey residue containing calomel and stannous chloride. Many metals also reduce mercury from the aqueous or alcoholic solution of the chloride. Most metals throw down calomel together with the mercury; but *zinc*, *cadmium*, and *iron* precipitate nothing but mercury, zinc being thereby converted into a semi-fluid amalgam, and cadmium forming an amalgam which crystallises in beautiful needles. For the other reactions of mercuric chloride in solution, see p. 900.

Compounds of Mercuric Chloride. a. With *Ammonia*.—When mercuric chloride is gently heated in a stream of ammoniacal gas, the latter is absorbed, and the compound fuses by the heat evolved in the combination. The product was found by Rose to contain $HhgCl^2.NH^3$. This compound boils at 590°, and may be distilled without loss of ammonia; it is decomposed by water.—(See MERCURY-BASES, AMMONIACAL).

β. With other *chlorides*.—Mercuric chloride unites with many other metallic chlorides, forming crystallisable double salts. They are prepared, for the most part, by mixing the aqueous solutions of the two salts in the required proportions, and crystallising by spontaneous evaporation.

Ammonium-salts.—One of these double salts has long been known as *sal alembroth*. It crystallises in flattened rhombic prisms, $2NH^4Cl.HhgCl^2.H^2O$, and is isomorphous with the corresponding potassium-salt. When exposed to dry air, it gives off its water without change of form. Kane has also obtained $NH^4Cl.HhgCl^2$, and the same with ½ at. water, $2(NH^4Cl.HhgCl^2).H^2O$, the first in a rhomboïdal form, and the second in long silky needles.—According to J. Holmes (Chem. News, v. 351) a solution of 25 pts. mercuric chloride and 1 pt. sal-ammoniac in hydrochloric acid deposits crystals of the salt $2NH^4Cl.9HhgCl^2$; and on mixing this solution with a very large excess of hydrochloric acid, or by dissolving in that acid a mixture of 3 pts. mercuric chloride and 1 pt. sal-ammoniac, the salt $2NH^4Cl.3HhgCl^2.4H^2O$ is obtained.

The *chlorides of barium* and *strontium* form well-crystallised compounds with mercuric chloride, viz. $BbaCl^2.HhgCl^2.4H^2O$, and $SsrCl^2.2HhgCl^2.2H^2O$. *Chloride of calcium* combines in two proportions with mercuric chloride. When the latter is dissolved to saturation in chloride of calcium, tetrahedral crystals separate from the solution, which are tolerably persistent in the air, and contain $CcaCl^2.5HhgCl^2.8H^2O$. After the deposition of these crystals, the liquid yields, when evaporated by a gentle heat, a second crop of large prismatic crystals, $CcaCl^2.2HhgCl^2.6H^2O$, which are very deliquescent.

The chlorides of *cobalt* and *copper* also form crystallisable double salts; chloride of *lead* does not appear to form a double salt with mercuric chloride.

The *iron-salt*, $FfeCl^2.HhgCl^2.4H^2O$, and the *manganese-salt*, $MmnCl^2.HhgCl^2.4H^2O$, are isomorphous and crystallise in rhombic prisms. An excess of mercuric chloride dissolves in the latter salt, and crystallises on cooling in large rhombic crystals.

Chloride of magnesium forms two double salts, with mercuric chloride, viz. $MmgCl^2.3HhgCl.H^2O$, and $MmgCl^2.HhgCl^2.6H^2O$, both deliquescent. *Chloride of nickel* gives two compounds, one of which crystallises in tetrahedrons, like the calcium-salt.

Potassium-salts.—When an aqueous solution of potassium-chloride is saturated at 30° with pulverised mercuric chloride, the liquid decanted, a quantity of potassium-chloride added equal to that already present, and the solution left to evaporate, the salt $2KCl.HhgCl^2.H^2O$ is deposited in large rhombic prisms. If the solution saturated at 30° be left to evaporate without further addition of chloride of potassium, another salt $KCl.HhgCl^2.H^2O$ is obtained in delicate asbestos-like crystals; and lastly, a solution of potassium-chloride heated to 60° and saturated with mercuric chloride, solidifies on cooling to a mass of slender needles having the composition $KCl.2HhgCl^2.2H^2O$.

The *sodium-salt* $NaCl.HhgCl^2.2H^2O$ crystallises in six-sided prisms.

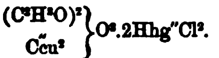
The *zinc-salt* has not been analysed. An aqueous solution of zinc-chloride containing excess of mercuric chloride deposits the latter, on evaporation, in large beautiful crystals, after which a double salt slowly separates in very deliquescent plates and needles. (Bonsdorff.)

Mercuric Chloride with Acid Chromate of Ammonium.—A solution of equal parts of these two salts yields, by concentration and cooling, large, shining, rose-coloured, six-sided prisms, of the salt $HhgCl^2.[NH^4CcrO^4.CcrO^3].H^2O$ (Richmond and Abel, Chem. Soc. Qu. J. iii. 202). The salt was discovered by Darby (Mem. Chem. Soc. i. 24), who however assigned to it a different formula. According to Zepharovich

(Wien. Akad. Ber. xxxix. 17) the crystals are monoclinic and exhibit the faces $oP . \infty P\infty . +\frac{1}{2}P\infty . -\frac{1}{2}P\infty . [P\infty] . [\frac{1}{2}P\infty] . \infty P . [\infty P2] . +P . +\frac{1}{2}P$. Ratio of axes $a : b : c = 0{\cdot}5087 : 0{\cdot}6462 : 1$. Angle of b and $c = 84^\circ\ 3'$; $\infty P : \infty P$ in the clinodiagonal principal section $= 76^\circ\ 42'$; $oP : \infty P = 98^\circ\ 41'$; $oP : [P\infty = 117^\circ\ 6'$; $oP : [\frac{1}{2}P\infty] = 135^\circ\ 38'$. Cleavage parallel to oP and $-\frac{1}{2}P\infty$.

The mother-liquor, from which this salt has separated, yields by further evaporation beautiful red needles of the salt, $\mathrm{\overline{Hg}Cl^2.[3(NH^4)^2\overline{Cr}O^4.\overline{Cr}O^3]}$. (Richmond and Abel.)

Mercuric chloride also forms double salts with the neutral and acid chromates of potassium, viz. $\mathrm{2\overline{Hg}Cl^2.K^2\overline{Cr}O^4}$ and $\mathrm{\overline{Hg}Cl^2.K^2\overline{Cr}O^4.\overline{Cr}O^3]}$. See CHROMATES (i. 938).

Mercuric Chloride with Basic Cupric Acetate.  $\left.\begin{matrix}\mathrm{(C^2H^3O)^2}\\ \overset{\prime\prime}{\mathrm{\overline{Cu}}}{}^2\end{matrix}\right\}\mathrm{O^4.2\overline{Hg}''Cl^2}$. This compound is produced, according to Wöhler, on mixing the solutions of mercuric chloride and neutral cupric acetate, saturated at ordinary temperatures, and leaving the mixture to itself for some time: it then separates in radiate hemispheric groups of crystals having a very fine deep blue colour. It is nearly insoluble in cold water, and is decomposed by boiling water.

Mercuric chloride also unites with *sulphide of ethyl*, forming the compound $\mathrm{(C^2H^5)^2S.\overline{Hg}Cl^2}$, already described (ii. 545); and with *sulphide of methyl*, forming a similar compound.

MERCURY, CYANIDE OF. See CYANIDES (ii. 253).

MERCURY, DETECTION AND ESTIMATION OF. 1. *Reactions in the dry way.*—Most mercury compounds are decomposed by heat, and give off metallic mercury; but mercurous chloride and bromide and mercuric chloride and iodide sublime undecomposed. All mercury-compounds, when thoroughly dried, intimately mixed with dry *carbonate of sodium*, and heated before the blowpipe in a tube closed at one end, are decomposed and give off metallic mercury, which condenses in the cold part of the tube. Those mercury-compounds which are volatile without decomposition, the chlorides for example, may escape decomposition by carbonate of sodium. In this case the mixture must be slightly moistened with water, the water expelled by gentle heating over the lamp, and removed with blotting paper, the tube being held horizontally to prevent the water from running down to the heated part. When the moisture is all expelled, the blowpipe flame is applied as before. This is an easy and certain method of detecting mercury. When the quantity of mercury present is very small, the sublimate which forms on the cold part of the tube may look, to the unassisted eye, like arsenic or antimony; but examination with a lens will show that it consists of minute liquid globules.

2. *Reactions in Solution.*

a. **Of Mercurous salts.** Normal or neutral mercurous salts are white; the basic salts are frequently yellow. Most of them are soluble in water, redden litmus, have a metallic taste, and do not act very violently on the animal body. All soluble mercurous salts are partially decomposed by water, a basic salt being precipitated and an acid salt left in solution; free acid redissolves the basic salt.

Sulphydric acid and *sulphide of ammonium* form with mercurous salts a black precipitate of mercurous sulphide $\mathrm{\overline{Hg}^2S}$, insoluble in sulphide of ammonium and in nitric acid, soluble in nitro-muriatic acid and in sulphide of potassium.

Hydrochloric acid and *soluble chlorides* form, even in very dilute solutions, a white precipitate of mercurous chloride, which is insoluble in dilute acids, and is blackened by potash or ammonia. Boiling nitric acid dissolves it; boiling hydrochloric acid decomposes it into mercuric chloride which dissolves, and metallic mercury, which remains as a grey powder.

Iodide of potassium forms a greenish-yellow precipitate of mercurous iodide (always, however, mixed with mercuric iodide) soluble in excess.

Cyanide of potassium separates metallic mercury, the mercurous cyanide $\mathrm{\overline{Hg}^2Cy}$, formed in the first instance, being resolved into mercuric cyanide, $\mathrm{\overline{Hg}Cy}$, and mercury.

Ferrocyanide of potassium forms a white; ferricyanide of potassium, a reddish-brown precipitate.

Phosphate of sodium and *oxalic acid* form white precipitates; *chromate of potassium*, a red; *gallic acid*, a brownish-yellow precipitate.

Mercurous salts are reduced by metallic *copper* and *zinc*, by *stannous chloride, ferrous sulphate, sulphurous acid*, and *phosphorous acid*, metallic mercury being separated as a grey powder.

All mercurous salts are converted into mercuric salts by boiling with *nitric acid*.

β. Of **Mercuric salts.** Normal mercuric salts (containing 2 at. of an acid radicle to 1 at. Hhg) are colourless; the basic salts are frequently yellow. They are violent acrid poisons, and have a disagreeable metallic taste. The normal salts redden litmus. Most of them are soluble in water. They are partially decomposed by water, with separation of a basic salt requiring free acid to dissolve it. The chloride, however, dissolves in water without decomposition; hence a solution of mercuric chloride differs in some of its reactions from that of the nitrate and of other salts which are partially decomposed by water. From their aqueous solutions, the mercury is, for the most part, precipitated in the metallic state by the same substances as from mercurous salts; but the complete reduction of the mercury is often preceded by the formation of a mercurous salt: such for example is the action of *phosphorous acid, sulphurous acid, stannous chloride,* metallic *copper,* &c. *Formic acid* reduces mercuric to mercurous chloride, and no excess of the reagent carries the reduction further, unless the solution be heated nearly to boiling. *Gold* does not by itself reduce mercury from its salts; but if a drop of a mercuric solution be laid on a piece of gold, and a bar of zinc, tin, or iron be brought in contact with the moistened surface, an electrolytic action is set up, and the gold becomes amalgamated at the point of contact.

Sulphydric acid and *alkaline sulphides,* added in excess to mercuric salts, throw down a black precipitate of mercuric sulphide, soluble in strong nitric acid. If, however, the quantity of the reagent added is not sufficient for complete decomposition, a white precipitate is formed, consisting of a compound of mercuric sulphide with the original salt, and often coloured yellow or brown by excess of the sulphide; this reaction is quite peculiar to mercuric salts.

Hydrochloric acid forms no precipitate in solutions of mercuric salts.

Ammonia and *carbonate of ammonium* form white precipitates, generally consisting of a mercurammonium salt. The *fixed alkalis* throw down a yellow precipitate of mercuric oxide (not hydrated), insoluble in excess. If, however, the solution contains a large quantity of free acid, no precipitate is formed, or only a slight one after a considerable time.

Carbonate of potassium or *sodium* throws down red-brown mercuric carbonate; but if any ammoniacal salt is present in the solution, the fixed alkalis and their carbonates throw down the white precipitate above mentioned. *Acid carbonate of potassium* or *sodium* also gives a brown-red precipitate with mercuric nitrate or sulphate; but with the chloride, it forms a white precipitate which afterwards turns red. The *carbonates* of *barium, strontium,* and *calcium* precipitate mercuric oxide from the solutions of the sulphate and nitrate, but not from the chloride.

Phosphate of sodium throws down white mercuric phosphate from the sulphate and nitrate, but not from the chloride. *Chromate of potassium* forms a yellowish-red precipitate.

Cyanide of potassium gives with mercuric nitrate a white precipitate soluble in excess: it does not precipitate the chloride.

Ferrocyanide of potassium forms, in solutions not too dilute, a white precipitate which gradually turns blue, prussian blue being formed, while the filtrate contains cyanide of mercury. *Ferricyanide of potassium* gives a white precipitate with the nitrate, no precipitate with the chloride.

Tincture of galls forms an orange-yellow precipitate with all mercuric solutions except the chloride.

Iodide of potassium produces a scarlet precipitate of mercuric iodide, soluble in excess either of the mercuric salt or of iodide of potassium.

3. *Quantitative Estimation.*

Mercury is generally estimated in the **metallic state**; sometimes, however, as **mercuric sulphide** HhgS, or as **mercurous chloride** HhgCl. To separate it from its compounds in the **metallic state**, it may be distilled with *quicklime* in a tube of hard glass sealed at one end. Into this tube is introduced, first a layer of carbonate of calcium, about an inch long; then the mixture of the substance with quicklime; lastly a layer of quicklime about two inches long, and a plug of asbestos to keep the lime in its place. The open end of the tube is next drawn out into a narrow neck, and bent at an obtuse angle. The tube is laid in a combustion-furnace, the same as that which is used for organic analysis, the neck being turned downwards and made to pass into a narrow-mouthed bottle containing water, so as to terminate just above the surface of the water. The tube is then gradually heated by laying pieces of red-hot charcoal round it, beginning at the part near the neck containing the pure quicklime. This portion having been brought to a full red heat, the heat is carefully extended towards the middle part, to decompose the compound and volatilise the mercury: any portion of the compound that may volatilise undecomposed will be decomposed in passing over the red-hot lime at the end. Lastly, the back part of the tube containing the carbonate is heated, so as to evolve carbonic anhydride and sweep out all the mercury vapour contained in the tube. The quantity of carbonic anhydride thus evolved may be increased by mixing the carbonate of calcium with acid carbonate of sodium. The mercury condenses under the water in the bottle, which must be kept cold. The water is poured off as completely as possible; the mercury transferred to a weighed porcelain crucible; the greater part of the water which still adheres to it removed by means of blotting-paper; the drying completed over sulphuric acid; and the mercury finally weighed.

Mercury may also be precipitated from its solutions in the metallic state by *stannous chloride* or by *phosphorous acid* at temperatures above 60°; the solution then decanted; the mercury washed with water, and dried in the manner just described.

If the mercury is mixed with a considerable quantity of organic matter, as in cases of mercurial poisoning, the organic matter may be destroyed by treatment with nitro-muriatic acid in a distillatory apparatus (i. 365), and the liquid subjected to the action of a voltaic current, the negative pole being composed of a plate of platinum or gold. The mercury then collects on this plate, and may be estimated by weighing the plate before and after the experiment.

The precipitation of mercury in the form of mercurous chloride is best effected by means of *hydrochloric acid* and *formate of potassium or sodium.* If the mercury is contained in an alloy, the alloy must be dissolved in nitromuriatic acid; if it is contained in solution in the form of mercuric nitrate, hydrochloric acid must be added, the solution, in either case, nearly neutralised with potash, the formate then added, and the whole exposed for some days to a temperature between 60° and 80° (at the boiling heat the mercury would be reduced to the metallic state). The mercurous chloride then precipitates, and must be collected on a weighed filter, washed, dried at a gentle heat, and weighed.

According to the latest experiments of H. Rose (Pogg. Ann. cx. 529), the best of all methods of estimating mercury is to precipitate it as calomel from the solution of mercuric chloride by *phosphorous acid*, either at ordinary temperatures or at a very gentle heat; if the temperature rises above 60° metallic mercury is precipitated.

Mercury is also frequently precipitated from its solutions, as a sulphide, by *sulphydric acid.* In that case, if the precipitate consists of the pure protosulphide, $HhgS$, as when it is thrown down from a solution of corrosive sublimate, the precipitate may be simply collected on a weighed filter, washed, dried over the water-bath, weighed, and the quantity of mercury thence determined. But if, as is generally the case, the precipitate also contains free sulphur, as when it is thrown down from a solution containing a ferric salt or a considerable excess of nitric acid; or if it be precipitated in conjunction with the sulphides of other metals, then the mercury must be separated from it by distillation with lime, as above described. Or again, the mixture of sulphides may be converted into chlorides by gentle heating in a stream of chlorine gas, the volatile chloride of mercury passed into water, and the mercury precipitated from the solution by stannous chloride.

The quantity of mercurous salt present in a solution may also be determined by precipitation with hydrochloric acid. The solution must, however, be very dilute, and be kept cool; it must also contain but a very small quantity of free nitric acid, as a larger quantity would convert the mercurous into mercuric chloride. To determine the proportions of mercurous and mercuric salt, when they exist together in solution, the mercurous salt is first precipitated with hydrochloric acid, and the remaining mercury by stannous chloride or sulphydric acid.

Volumetric methods. C. W. Hempel (Ann. Ch. Pharm. cx. 176) estimates mercury in the form of mercurous chloride, by means of a standard solution of iodine in iodide of potassium, which dissolves it in the form of potassio-mercuric iodide:

$$HhgCl + 3KO + I = 2KI.HhgI^2 + KCl.$$

The quantity of iodine used is estimated by a graduated solution of hyposulphite of sodium (i. 265), and the quantity of mercury is thence calculated.

Another method given by Hempel (Ann. Ch. Pharm. cvii. 98) consists in agitating the mercurous chloride with dilute sulphuric acid and *permanganate of potassium* till it is dissolved, and estimating the quantity of permanganate used for the purpose by means of a standard solution of oxalic acid.

When the mercury is in solution as a mercuric salt, it is precipitated as calomel by ferrous sulphate, or by any of the other methods above given.

4. *Separation of Mercury from other Metals.*

Mercury may be separated from all other metals, except arsenic and antimony, by its superior volatility. When it exists in the form of an amalgam, the compound is simply heated, and the quantity of mercury determined by the loss of weight. If it exists as an oxide, chloride, &c., combined with compounds of other metals, it may be separated by distillation with *quicklime*, as above described. Its separation from the alkali and earth-metals, and from uranium, manganese, nickel, cobalt, iron zinc, and chromium, may also be effected by precipitation with *sulphydric acid*. From bismuth and cadmium it may be separated by reduction with *stannous chloride;* from copper, by mixing the solution with excess of *cyanide of potassium*, and passing sulphydric acid through the liquid, whereby the mercury is precipitated as sulphide, while the copper remains dissolved; from lead, by precipitating that metal with *sulphuric acid*, with addition of alcohol (H. Rose), the sulphuric acid being added in excess, as otherwise a basic sulphate of mercury may be precipitated at the same time. From arsenic, tin and antimony, mercury is separated by the solubility of the sulphides of those metals in sulphide of ammonium.

Field (Chem. Soc. J. xii. 32) separates mercury from antimony, by digesting the precipitated sulphides with moderately strong *hydrochloric acid*, which dissolves the sulphide of antimony and leaves the sulphide of mercury.

From silver, mercury, if in the form of a mercuric salt, is easily separated by *hydrochloric acid*, which precipitates the silver alone as chloride. If the mercury is in the form of a mercurous salt, the two metals are precipitated together as chlorides, and the separation is then easily effected by *ammonia*, which dissolves the chloride of silver, and blackens the mercurous chloride; or they may be separated by *nitromuriatic acid*, in the cold, which dissolves the chloride of mercury, leaving the chloride of silver undissolved.

When mercury, silver, and lead occur together in a solution, it is best to bring all the mercury to the state of mercuric salt by boiling with nitric acid: the silver may then be precipitated by *hydrochloric*, and the lead by *sulphuric acid*. Or the separation may be effected by *cyanide of potassium*, the solution being first nearly neutralised by an alkaline carbonate, and cyanide of potassium added in excess. The addition of nitric acid throws down the whole of the silver as cyanide, leaving the mercury in solution as cyanide, and the lead as nitrate, from which the lead may be precipitated by an alkaline carbonate.

For the analysis of a mixture of mercuric oxide, cinnabar, and red lead, Wöhler recommends the following process: The mixture is digested with *nitric acid*, which dissolves the mercury as mercuric oxide, and resolves the red lead into protoxide, which dissolves, and dioxide, which remains undissolved (p. 553), the cinnabar being also left undissolved. The lead is precipitated from the solution by dilute sulphuric acid, and then the mercury by sulphydric acid or stannous chloride. The residue is then treated on the filter with a mixture of warm nitric and oxalic acids, which dissolves out the dioxide of lead, and the residual cinnabar is washed, dried, and weighed.

The separation of mercury from gold in solution, may be effected by precipitating the gold in the metallic state by warming the solution with *oxalic acid* (ii. 928), and afterwards adding hydrochloric acid to redissolve the oxalate of mercury, precipitated at the same time. If the hydrochloric acid were added at an earlier stage of the process, it would greatly retard the precipitation of the gold. The mercury must of course be in the mercuric state.

5. *Atomic weight of Mercury.*

The atomic weight of this metal was for many years estimated, according to the experiments of Sefström, made in 1812 (Schw. J. xxii. 328), at 101·26 for Hg′, or 202·52 for Hhg″. Turner, however, in 1835 (Ann. Ch. Pharm. xiii. 14), by the analysis of mercuric oxide and chloride, obtained lower numbers, viz. from 200 to 200·3, and his results have been confirmed by the experiments of Erdmann and Marchand in 1844 (*ibid.* lii. 216). These chemists decomposed carefully prepared and dried mercuric oxide by ignition in a stream of dry carbonic anhydride; absorbed the liberated oxygen (part of which would otherwise recombine with the mercury) by ignited charcoal and copper; and collected the mercury which distilled over, the escaping gases being finally freed from mercury by passing through a tube containing gold-leaf. In five experiments, in each of which from 44 to 118 grms. mercuric oxide, $HhgO^2$, were decomposed, they found from 92·594 to 92·604 per cent. mercury; mean 92·597 per cent. Hence the value of Hhg is between 200·05 and 200·33; mean 200·14. It is usual to take as the true atomic weight of mercury, Hg = 100, or Hhg = 200.

The vapour-density of mercuric chloride, which, according to the observations of Mitscherlich, is 9·8, gives a condensation to 1 vol. for the formula HgCl, and of 2 vols. for $HhgCl^2$ (p. 897). This result affords an argument in favour of the larger atomic weight and the diatomicity of mercury in the mercuric compounds, and we shall presently see that this view is further corroborated by the constitution of the organic compounds of mercury.

MERCURY, ETHIDE OF. See Mercury-radicles, Organic.

MERCURY, FLUORIDES OF. Mercury forms two fluorides, corresponding in composition with the chlorides.

Mercurous Fluoride. Hg^2F or $HhgF$. Berzelius obtained this compound as a sublimate, mixed with mercurous chloride, by heating the latter with fluoride of sodium. It has been further examined by Finkener (Pogg. Ann. cx. 142), who obtains it by adding recently precipitated calomel to a solution of silver-fluoride (prepared by digesting silver-carbonate with hydrofluoric acid); the whole of the silver is then gradually precipitated, and the liquid evaporated over the water-bath, yields small yellow crystals of mercurous fluoride. An easier mode of preparation is to add recently precipitated mercurous carbonate to hydrofluoric acid, which dissolves it completely at first, with evolution of carbonic anhydride, but on addition of a larger quantity deposits mercurous fluoride as a heavy, light yellow, crystalline powder. From a solution in excess of hydrofluoric acid, it is deposited in indistinct (apparently cubic) crystals.

Mercurous fluoride is partly dissolved by water, partly decomposed into mercurous oxide and hydrofluoric acid. It is blackened even by moist air, especially if exposed to light. It is also decomposed when heated above 260° in dry air, mercury subliming, and the glass vessel becoming corroded. From the solution of the compound in hydrofluoric acid, *potash* throws down mercurous oxide; *ammonia*, a black precipitate containing metallic mercury and quickly turning grey, while the filtered liquid contains mercuric oxide and soon deposits a white mass containing mercury, ammonia, and fluorine. Dry mercurous fluoride is decomposed in like manner, by the prolonged action of aqueous *ammonia*, into metallic mercury and a mercuric compound. It slowly absorbs ammonia gas, turning black and being converted into fluoride of mercurosammonium $(NH^3Hhg')F$.

Mercurous Silicofluoride.—$HhgSiF^6.H^2O$ is deposited from the solution of mercurous carbonate in hydrofluosilicic acid, in transparent, colourless, prismatic crystals. (Finkener.)

Mercuric Fluoride. HgF or $Hhg''F^2$. Mercuric oxide added to hydrofluoric acid is converted into an orange-yellow powder, consisting of an oxyfluoride, and by repeatedly treating this compound with hydrofluoric acid, mercuric fluoride is deposited as a white crystalline mass containing $HhgF^2.2H^2O$. The same product is obtained by adding dry mercuric oxide to a large excess of aqueous hydrofluoric acid (containing about 50 per cent. HF) (Finkener, Pogg. Ann. cx. 628). According to Frémy (Ann. Ch. Phys. [3] xlvii. 5), mercuric fluoride is obtained in long colourless hydrated needles (frequently, however, contaminated with hydromercuric fluoride or mercuric oxyfluoride) by slowly evaporating a solution of mercuric oxide in excess of hydrofluoric acid. Finkener, however, did not obtain crystals in this manner.

Hydrated mercuric fluoride decomposes at 50°, giving off hydrofluoric acid together with water, and leaving the oxyfluoride. It is permanent in dry air at ordinary temperatures, but is decomposed by *water*, yielding mercuric oxyfluoride and a solution of hydrofluoric acid containing a small quantity of mercuric oxide. A solution of mercuric fluoride in hydrofluoric acid mixed with a slight excess of *ammonia*, deposits, after some time in the cold, and immediately when heated, a white gelatinous precipitate, which, when washed and dried over sulphuric acid, consists of ammonio-mercuric oxyfluoride $2NH^3.Hhg^2F^2O$. (Finkener.)

Mercuric Silicofluoride and *Silico-oxyfluoride.*—A solution of mercuric oxide in hydrofluosilicic acid yields by evaporation small pale yellow needles, which were regarded by Berzelius as mercuric silicofluoride; but according to Finkener they consist of a silico-oxyfluoride $Hhg''Si^{iv}Fl^6.Hhg''O.3H^2O$. This compound is resolved by water, even at ordinary temperatures, into a soluble acid salt and an insoluble yellow pulverulent basic salt.

A solution of mercuric oxide in hydrofluosilicic acid, concentrated so far that oxysilicofluoride begins to separate, and then left to itself at a temperature below 15°, yields colourless rhombohedral crystals grouped like steps, probably consisting of hydrated mercuric silicofluoride $Hhg''Si^{iv}F^6.6H^2O$. They are very unstable and deliquesce when slightly heated, but effloresce over sulphuric acid. (Finkener.)

A double salt of mercuric fluoride with *fluoride of ammonium* is produced, according to Berzelius, by treating mercuric fluoride with aqueous ammonia.

MERCURY, IODIDES OF. Mercury unites with iodine in three or four proportions, forming a mercurous and mercuric iodide analogous to the chlorides also a mercuroso-mercuric iodide, and perhaps a periodide. The two elements unite directly, the combination, when large quantities are employed, being attended with considerable rise of temperature.

Mercurous Iodide. Hg^2I or $HhgI$.—This compound is produced by triturating 200 pts. mercury with 127 pts. iodine or 454 pts. mercuric iodide, with addition of a little alcohol, and removing any mercuric iodide that may be formed in the first instance, or remain unacted upon in the second, by solution in alcohol, which leaves the mercurous iodide undissolved. It may also be obtained by precipitating a mercurous salt with iodide of potassium. The acetate is best adapted to the purpose, yielding at once pure mercurous iodide. When the nitrate is used, the precipitate is frequently contaminated with mercuric iodide, either formed directly from mercuric nitrate in the solution, or by the oxidising action of free nitric acid in the solution on the precipitated mercurous iodide.

Mercurous iodide is a greenish-yellow powder of specific gravity 7·65 to 7·75. It is very sparingly soluble in *water*, quite insoluble in *alcohol*; *ammonia* dissolves it partially, leaving a grey residue. Mercurous iodide is very unstable, being easily resolved, under various circumstances, into metallic mercury and mercuric or mercuroso-mercuric iodide. When *heated*, it yields a sublimate of metallic mercury and mercuroso-mercuric iodide. When treated with *hydriodic acid* or with solutions of *iodide of potassium* or other metallic iodides, it is resolved into mercury and mercuric iodide, which unites with the other iodide, forming a soluble salt. In the moist state it is decomposed and blackened by exposure to *light*.

Mercurous iodide is used in medicine, and in preparing it for that purpose the greatest care must be taken to insure its perfect freedom from mercuric iodide, which is a violent poison. To test its freedom from this admixture, W. Squire (Jahresb. 1862, p. 217) heats it with *aniline*, whereupon, if it contains mercuric iodide, the well-known magenta colour is produced, whereas if the mercurous iodide is quite pure, no coloration takes place.

Mercuroso-mercuric Iodide. $Hhg^2I^3 = HhgI.HhgI^2$.—Prepared by precipitating mercurous nitrate with iodide of potassium, the precipitate not being collected till it has acquired a yellow colour. According to Boullay, it is best to mix the solution of potassium-iodide with $\frac{1}{2}$ at. iodine, in which case mercuroso-mercuric iodide is precipitated at once. The compound may also be obtained by triturating mercuric iodide with one-third as much mercury as it already contains ($3HhgI + Hhg = 2Hhg^2I^3$).

Mercuroso-mercuric iodide is a yellow powder which when heated turns red, melts, and may be sublimed without alteration. The sublimed crystals have a dark carmine-red colour while hot, but become yellow on cooling (Inglis, Colin). The compound is insoluble in *water* and in *alcohol*, the latter not extracting any mercuric iodide from it. It remains unaltered when kept in the dark; but becomes dark coloured on exposure to light. *Hydriodic acid* and solutions of *iodides* first resolve it into mercurous and mercuric iodide, the latter uniting with the soluble iodide, and afterwards decompose the mercurous iodide itself, as above described, with separation of metallic mercury. (Boullay.)

Mercuric Iodide. HgI or $Hhg''I^2$.—This compound may be produced by triturating 1 at. mercury with 2 at. iodine (200 pts. mercury to 254 iodine), moistened with alcohol; according to Mohr, however, the combination of two elements in this way is never complete, the product always containing a certain portion of free iodine which escapes during the drying over the water-bath, also some mercurous iodide which is resolved by sublimation into mercuric iodide and metallic mercury. Dublanc pours 1 kilogramme of alcohol on 100 grammes of mercury, and adds 124 grms. iodine in successive portions of 10 grms. each, stirring after each addition till the alcohol has become colourless. After the last 4 grms. of iodine have been added, the liquid becomes permanently coloured, in consequence of the complete conversion of the mercury into mercuric iodide; the product is washed with alcohol. Mercuric iodide is, however, best prepared by precipitating mercuric chloride with iodide of potassium, or iodide of iron: *a.* 8 pts. mercuric chloride and 10 pts. iodide of potassium are dissolved in separate portions of water, the solutions mixed and the resulting precipitate collected and carefully washed. *β.* 2 at. iodine immersed in water are converted into ferrous iodide by addition of iron-turnings; the resulting solution is immediately mixed with a solution 1 at. mercuric chloride ($HhgCl^2$), and the precipitated mercuric iodide is quickly separated from the liquid, to prevent it from being contaminated with the basic ferric chloride which is gradually deposited from the solution.

Mercuric iodide thus obtained is a powder of a splendid scarlet colour, very slightly soluble in *water*, more soluble in *alcohol*, especially when hot, somewhat soluble also in *ether*. It dissolves easily in aqueous *iodide of potassium*, and crystallises from the solution in beautiful red quadratic octahedrons, also in the combinations P . oP, ∞P∞ . oP . P, and ∞P∞ . oP. Length of principal axis = 1·997. Angle P : P in the terminal edges = 96° 24′; in the lateral edges 141° 0′. Cleavage perfect parallel to oP. Specific gravity = 6·2009 (Karsten); 6·320 (Boullay); 5·91 (Schiff).—The red iodide turns yellow when gently heated, melts at a higher temperature, and sublimes in bright yellow rhombic prisms exhibiting the combination

$\infty P . oP$, and having the angle $\infty P : \infty P = 66°$ (*Kopp's Krystallographie*, pp. 160, 257). Mercuric iodide is therefore dimorphous, and exhibits a red colour in one of its forms, a yellow colour in the other. The red modification is much more stable than the yellow; in fact the yellow crystals, even when left to themselves at ordinary temperatures, gradually recover their original colour and crystalline structure, being converted into an aggregate of the red crystals; the same change takes place instantly when the yellow crystals are pressed, rubbed, or scratched. The yellow iodide retains its colour longest when it has been prepared by subjecting the pulverised red iodide to a moderate heat. The yellow crystals obtained by sublimation often turn red on cooling, in consequence of the friction or agitation resulting from the contraction of the glass vessel, or of the crystals themselves (Mitscherlich). Mercuric iodide precipitated from the solution of the chloride by iodide of potassium, is likewise yellow at the first instant of precipitation, but quickly turns red, even while immersed in the liquid. In this case the course of the alteration may be easily watched under the microscope—yellow rhombic laminæ being observed in the first instance, which continually diminish in bulk, becoming truncated on their edges and angles, and ultimately disappearing, while red quadratic octahedrons appear in their place (Warington). The solutions of mercuric iodide in alcohol ether, aqueous iodide of potassium, &c., are colourless, and may therefore be supposed to contain the yellow modification; if, however, the iodide separates slowly from them in crystals, these crystals are red; but if the separation takes place rapidly, as for example when the alcoholic solution is poured into water, the iodide is yellow at the first instant of separation, but very soon turns red. According to Reynoso (Compt. rend. xxxix. 696), an alcoholic solution of the iodide which has been kept for some time gives immediately a red precipitate with water. Schiff (Ann. Ch. Pharm. cxi. 371), on the other hand, found that an alcoholic solution which had been kept for fifteen months, still gave a yellow precipitate with water; and the yellow crystals which formed in it likewise remained unaltered in colour. Schiff also finds that the alcoholic solution, when mixed with water, first becomes quite milky, and after a few hours deposits shining yellow rhombic plates with angles of 114° 30′ and 65° 30′, and exhibiting beautiful coloured spectra under the polarising microscope.

Potassium triturated with mercuric iodide, abstracts the iodine with incandescence. A similar action is exerted by many of the heavy metals on trituration, either alone or with water, the resulting iodide sometimes uniting with the iodide of mercury to form a double salt; *zinc* and *tin* form amalgams with the liberated mercury. [For the behaviour of the individual metals, see *Gmelin's Handbook*, vi. 38.] When mercuric iodide is boiled with aqueous *potash*, mercuric oxide separates, and a yellow solution is formed containing a potassio-mercuric iodide, $2KI.3HhgI^2$:

$$4HhgI^2 + 2KHO = HhgO + 2KI.3HhgI^2 + H^2O,$$

which, on cooling, first deposits mercuric oxide, and then greenish-yellow needles of $KI.HhgI^2$. Alcoholic potash acts in like manner and more easily. *Soda*, *baryta*, and *strontia* likewise act in a similar manner, producing double iodides; *lime*, *carbonate of potassium*, and *carbonate of sodium* do not decompose mercuric iodide when boiled with it in water; but if alcohol be substituted for the water, decomposition takes place, the alcohol appearing to favour the action by its solvent power. Mercuric iodide dissolves in aqueous *hypochlorite of calcium* when the solution is heated; and as it begins to boil, deposits periodate of calcium in the form of a white jelly, while mercuric chloride remains dissolved (Rammelsberg). When *chlorine gas* is passed into water in which mercuric iodide is suspended, a bright yellow solution is formed, containing mercuric chloride and trichloride of iodine. (Filhol.)

Double salts of Mercuric Iodide.—Mercuric iodide unites with the more positive metallic iodides, forming a series of double salts, Bonsdorff's iodohydrargyrates, which have been particularly studied by Boullay (Ann. Ch. Phys. [2] xxxiv. 345). They are obtained, for the most part, by dissolving mercuric iodide in the solution of the positive iodide, and evaporating the solution. Mercuric iodide likewise forms double salts with metallic chlorides.

Ammonio-mercuric Iodide, $(NH^4)^2HhgI^4.3H^2O$, or $2NH^4I.HhgI^2.3H^2O$, separates in yellow needles from a hot solution of mercuric iodide in iodide of ammonium, after pure mercuric iodide has been previously deposited. When heated, it melts and sublimes, partly unaltered, partly decomposed. Water separates mercuric iodide from it. (Boullay.)

Baryto-mercuric Iodide.—A solution of mercuric iodide in aqueous iodide of barium, after being freed from excess of mercuric iodide by cooling and dilution, deposits yellow crystals, soluble in water, which, according to Boullay, have probably the composition $BaHgI^2$, or $Bba''Hhg''I^4$. A hot saturated solution of mercuric iodide in iodide of barium deposits, on cooling, a portion of the mercuric iodide, and the mother-liquid yields by evaporation, crystals apparently consisting of $BbaHhg^2I^6 = BbaI^2.2HhgI^2$. The crystals decompose when dried at a high temperature, or when dissolved in a large quantity of water, mercuric iodide separating. (Boullay.)

Cadmio-mercuric Iodide is obtained by triturating cadmium-filings with moist mercuric iodide, and exhausting with water. Crystallises in small, yellowish-white very soluble laminæ. (Berthemot.)

Calcio-mercuric Iodide. $CcaI^2.2HhgI^2$?—Obtained like the corresponding barium-salt, and decomposed in a similar manner by water.

Ferroso-mercuric Iodide.—The saturated solution of mercuric iodide in ferrous iodide yields, by evaporation over sulphuric acid, yellow-brown prisms, which quickly oxidise in contact with the air (v. Bonsdorff). A hot saturated solution of the two salts yields, after deposition of a portion of the mercuric iodide, brownish-yellow, very deliquescent needles, which are decomposed by water, and dissolved by strong acetic acid and by alcohol. (Berthemot.)

Magnesio-mercuric Iodide.—A hot saturated solution of mercuric iodide in iodide of magnesium, deposits mercuric iodide on cooling; and the remaining liquid yields greenish-yellow, needle-shaped crystals, which probably consist of $MmgI^2.2HhgI^2$, and are resolved by water into mercuric iodide, and a solution apparently containing $MmgI^2.HhgI^2$. (Boullay.)

Potassio-mercuric Iodide.—A concentrated solution of iodide of potassium takes up, at the boiling heat, 3 at. $HhgI^2$ to 2 at. KI; and of the 3 at. mercuric iodide, 1 at. is deposited on cooling, while the mother-liquor deposits the compound $2(KI.HhgI^2).3H^2O$ in long yellow prisms. The crystals, when heated, first give off water, and then melt to a red liquid, from which mercuric iodide separates. They are soluble in alcohol and in ether, but water decomposes them, separating about half the mercuric iodide, and the liquid then yields by evaporation a saline mass, which may be regarded as $2KI.HhgI^2$ (Boullay). Dilute acids decompose the crystals, separating the mercuric iodide. Potassio-mercuric iodide is likewise easily produced by boiling a solution of potassium-iodide with mercuric oxide.

Sodio-mercuric Iodide.—Iodide of sodium reacts with mercuric iodide in a similar manner to iodide of potassium. The solution, after depositing 1 at. mercuric iodide, yields by evaporation, a yellow, non-crystallising mass, which turns red when rubbed or scratched, from separation of mercuric iodide.

Strontio-mercuric Iodide, prepared like the corresponding barium-compound, forms yellowish needles.

Zinco-mercuric Iodide, prepared by Bonsdorff, crystallises in yellow, very deliquescent, rhombic prisms.

Periodide of Mercury, HgI^2, or $HhgI^4$? is obtained, according to Hunt, by precipitating aqueous mercuric chloride with a solution of potassium-iodide previously saturated with iodine. It forms a purple-red powder, which is resolved into mercuric iodide and free iodine by heating or by exposure to the air. Gmelin regards it as a mixture of mercuric iodide with iodine.

MERCURY, IODOCHLORIDE OF.—$\overset{\prime\prime}{H}hg^3I^2Cl^4$.—This compound is produced on dissolving mercuric iodide in a hot solution of corrosive sublimate, and separates on cooling in white, jagged, fern-like laminæ (Liebig). According to Boullay, a hot saturated solution of mercuric iodide in corrosive sublimate yields on cooling a yellow powder, $Hhg''ICl$; a less saturated solution yields, after the yellow powder, pale-yellow crystals, which, as well as the powder, soon turn red, from separation of mercuric iodide.

MERCURY, IODOSULPHIDE OF. See MERCURY, SULPHIODIDE OF (p. 915).

MERCURY, MERCAPTIDE OF. Syn. with Sulphethylate of mercury. See ETHYL, SULPHYDRATE OF (ii. 548).

MERCURY, METHIDE OF. See MERCURY-RADICLES, ORGANIC (p. 921).

MERCURY, NITRIDE OF. Hg^3N, or $\overset{\prime\prime}{H}hg^3N^2$. See TRIMERCURAMINE, under MERCURY-BASES, AMMONIACAL (p. 917).

MERCURY, OXIDES OF. Mercury unites with oxygen in two proportions, forming the mercurous and mercuric oxides, analogous in composition to the chlorides.

Mercurous Oxide. Hg^4O, or Hhg^2O. *Black oxide of mercury* (also called *dioxide* and *suboxide* of mercury). It is produced by treating mercurous chloride, or the solution of a mercurous salt, with excess of caustic alkali. To preserve it from decomposition, it must be washed and dried in the dark. Donovan suspends finely-divided calomel in water, treats it at once with excess of potash, and then washes and dries the product. The mercurous oxide thus obtained yields but few globules of mercury on trituration; but if too little potash be added in the first instance, there is formed, according to Donovan, a mercurous oxychloride; and on further addition of potash, a mixture of mercurous oxide, mercuric oxide and metallic mercury. According to Guibourt (Ann. Ch. Phys. [2] i. 422], it is impossible to obtain this oxide pure, because, during washing, even in the dark, it is partly resolved into a mixture of mercuric oxide and metallic mercury. The product formed by triturating mercuric oxide with mercury is merely a mixture.

Mercurous oxide is a brown-black powder, destitute of taste and smell. The specific gravity of that obtained from calomel by the action of caustic potash is 8·9503 (Karsten), 10·69 (Herapath). It is very unstable, being resolved, even on exposure to diffused *daylight*, or by slight trituration in a mortar, into mercuric oxide and metallic mercury. At a *red heat*, it is resolved into mercury and oxygen-gas. With aqueous *phosphorous acid*, it yields mercury and phosphoric acid. By *potassium* and *sodium*, at about the melting points of those metals, it is decomposed, with vivid ignition and slight detonation, yielding metallic mercury and an alkali. It detonates when struck with *phosphorus*. It is slowly decomposed by *phosphoretted hydrogen gas* (Graham). When boiled with aqueous *iodide of potassium*, it yield, metallic mercury and potassio-mercuric iodide; if the mercurous oxide is in excess mercurous iodide is formed at the same time (Berthemot, J. Pharm. xiv. 189). A concentrated solution of *sal-ammoniac* decomposes it in a similar manner, ammonia being evolved, and mercury being separated, together with mercuric chloride (Pagenstecher, Repert. Pharm. xxvii. 27; L. Thompson, Phil. Mag. [3] x. 179). *Carbonate of ammonium* likewise decomposes mercurous oxide into mercuric oxide and metallic mercury.

Mercurous salts.—Mercurous oxide dissolves in acids, forming the mercurous salts, which may also be produced by dissolving mercury, under particular conditions, in certain oxidising acids, such as nitric or sulphuric acid; also in some cases by precipitation.

The normal mercurous salts have the composition $Hg^{2n}A_n$ or Hhg^nA_n, the symbol A_n denoting an *n*-atomic acid or chlorous radicle, such as $\acute{N}O^3$, $\overset{\prime\prime}{S}O^4$, &c., and Hg (= 100) being hemi-atomic, and Hhg (= 200) monatomic in these salts, *e.g.*,

Mercurous nitrate = Hg^2NO^3 or $HhgNO^3$
Mercurous sulphate = $Hg^4(SO^4)''$ or $Hhg^2(SO^4)''$.

These salts may also be regarded as compounds of mercurous oxide with anhydrides, or acid oxides, *e.g.* the nitrate, as $Hhg^2O.N^2O^5$.

There are also basic mercurous salts, which may be regarded either as compounds of the normal salts with mercurous oxide, or as oxy-salts, analogous to the oxychlorides &c.; or again as formed on the type of two or more molecules of water, in which more than half the hydrogen is replaced by mercury, *e.g.*,

$$2Hhg^2O.N^2O^5 \quad = \quad Hhg^2O.2HhgNO^3 \quad = \quad Hhg^4\left\{\begin{matrix}(NO^3)^2\\ O\end{matrix}\right. \quad = \quad \left.\begin{matrix}(NO^2)^2\\ Hhg^4\end{matrix}\right\}O^3.$$

$$3Hhg^2O.N^2O^5 \quad = \quad 2(Hhg^2O.HhgNO^3) \quad = \quad Hhg^3\left\{\begin{matrix}NO^3\\ O\end{matrix}\right. \quad = \quad \left.\begin{matrix}NO^2\\ Hhg^3\end{matrix}\right\}O^2.$$

For the properties and reactions of mercurous salts see p. 899.

Mercuric Oxide. Hg^2O or $HhgO$. *Red oxide of mercury* (also called *bioxide* and *deutoxide* of mercury). This oxide was known to the Arabians in the eighth century. Geber and afterwards Raimond Lullius showed how to prepare it by igniting mercury-nitrate; and Boyle, towards the end of the seventeenth century, discovered that it may be prepared by heating mercury in contact with the air.

Preparation.—1. By keeping mercury for a month or longer at a boiling heat in a flask filled with air, and having a long loosely-fitting tube adapted to its mouth: the oxide thus obtained is called in pharmacy, *Mercurius præcipitatus per se.*—2. By exposing mercuric or mercurous nitrate to a high and gradually increasing temperature in a crucible, or, better, in a glass vessel surrounded with sand, as long as nitrous acid is evolved. To save nitric acid, the nitrate, moistened with water, may be previously triturated with an equal weight of mercury, till the latter is completely deadened: this preparation is called *Mercurius præcipitatus ruber.* Care must be taken not to raise the temperature too high. The oxide prepared by this process on the small scale is a dull powder; in commerce, it occurs in shining crystalline grains. According to Gay-Lussac, the small unpulverised crystals of mercurous nitrate yield the second form of the oxide, but the pulverised salt yields the first form. The more perfect crystallisation of the oxide prepared on the large scale is undoubtedly due to the slower rate at which the heat increases.—3. By precipitating a dissolved mercuric salt with excess of potash, and washing the precipitate.

Impurities and Adulterations.—1. *Basic mercuric nitrate*, when the salt has not been sufficiently heated. The oxide containing this salt gives off nitrous vapours when gently heated in a retort. It may be purified in this manner, or by boiling with potash-ley, or by washing with water.—2. *Nitre.* May be completely removed by boiling-water.—3. *Minium.* Remains in the form of fused protoxide of lead, when the mercuric oxide is strongly heated in a glass tube, or in the form of peroxide of lead, when the mercuric oxide is dissolved in nitric acid.—4. *Brick dust.* Remains behind, when the oxide is ignited or dissolved in nitric acid.—5. *Cinnabar.* Remains, when the oxide is dissolved in hydrochloric acid.

Properties.—Pure mercuric oxide is generally crystallo-granular and scaly, shining and of a bright brick-red colour; by pulverisation it acquires an orange-yellow colour, lighter as the powder is finer. When prepared on the small scale, it is a dull, flocculent, earthy mass or powder, of a brownish brick-red colour. When obtained by precipitating a mercuric salt with an alkali, it forms a light orange-yellow powder. Specific gravity: 11·000 (Pol. Boullay), 11·074 (Herapath), 11·1909 (Karsten), 11·29 at 4° in vacuo (Royer and Dumas), 11·136 (Playfair and Joule).—When heated, it becomes vermillion-red, and afterwards violet black, but recovers its original colour on cooling. It has a repulsive metallic taste, and is a violent acrid poison.

The precipitated yellow oxide is more readily decomposed by heat and by chlorine than the red oxide obtained by the first or second method. The difference is attributed by Pelouze (Compt. rend. xvi. 50) to the difference of aggregation of the two varieties, the precipitated oxide being amorphous and the calcined oxide crystalline; but Gay-Lussac (*ibid.* xvi. 309) has shown that the difference is mainly due to the more finely divided state of the precipitated oxide; chlorine acts less readily on the calcined oxide, because the smaller surface presented by the latter quickly becomes covered with mercuric chloride, which impedes the further action of the chlorine; but if the two varieties of the oxide are subjected to the action of chlorine under water, which dissolves the mercuric chloride as fast as it is formed, no difference in the rate of action on the two can be perceived. The yellow as well as the red oxide is anhydrous.

Mercuric oxide is not quite insoluble in water; according to Wallace (Chem. Gaz. 1858, p. 345) 1 pt. of it dissolves in 200,000 pts. of cold water after long standing, and in 125,000 pts. after boiling and cooling of the liquid. The solution has a strong metallic taste; turns violet juice green; becomes covered on exposure to the air with shining films of metallic mercury; is turned brown by sulphydric acid, and milky by ammonia. (Guibourt, Donovan.)

Decompositions.—Mercuric oxide gradually turns black when exposed to *sunshine*, being superficially decomposed into oxygen and metallic mercury, according to Guibourt, or, according to Donovan, into oxygen and mercurous oxide. At a *red heat*, it volatilises completely, being resolved into oxygen gas and vapour of mercury. Part of the mercurial vapour again takes up oxygen, and the oxide thus formed collects on the surface of the mercury which passes over, and diminishes its fluidity. With *phosphorus*, mercuric oxide detonates under the hammer. Boiled with phosphorus and water, it yields phosphide of mercury and aqueous phosphoric acid (Pelletier); at ordinary temperatures, the same mixture yields fluid mercury and phosphoric oxide, no phosphoric or phosphorous acid dissolving in the water (Braamcamp and Siqueira). A phosphate is likewise formed at the same time (Gmelin). Aqueous *phosphorous acid* forms mercury and aqueous phosphoric acid (Braamcamp and Siqueira). Mercuric oxide mixed with *sulphur*, and heated in a retort, produces a tremendous explosion (Proust). Concentrated *sulphurous acid* boiled with this oxide, immediately converts it into fluid mercury, with formation of sulphuric acid. At ordinary temperatures, smaller quantities of sulphurous acid produce a rise of temperature amounting to 7·5°, and form a white powder, consisting of mercurous sulphate, part of which dissolves in the liquid. An excess of sulphurous acid turns this powder grey, and reduces it very slowly, but completely, to metallic mercury. So long as this change remains incomplete, the liquid still retains mercury, but is not rendered turbid by addition of common salt; nevertheless, it gives a precipitate with sulphide of ammonium, and after long standing, or immediately on boiling, deposits metallic mercury in the form of a grey powder; the precipitation of the mercury is complete, provided the quantity of sulphurous acid is not too small (A. Vogel). *Potassium* or *sodium* heated to the melting point, decomposes mercuric oxide with vivid combustion and slight detonation, yielding metallic mercury and alkali. (Gay-Lussac and Thénard.) *Zinc* and *tin* filings, and pulverised *antimony* heated with mercuric oxide, likewise occasion fiery decomposition. Solution of *stannous chloride* poured upon mercuric oxide reduces it to the metallic state, and is itself converted into stannic chloride, part of which is precipitated in the form of a basic salt, the action being attended with a rise of temperature amounting to 60° (A. Vogel). *Hydrated ferrous oxide* converts mercuric into mercurous oxide; so likewise do ferrous salts (Duflos, Schw. J. lxv. 115). Heated solution of *sugar* reduces mercuric to mercurous oxide (A. Vogel). *Chlorine gas* decomposes mercuric oxide at a red heat, the products being oxygen gas and mercuric chloride; at lower temperatures, hypochlorous acid and mercuric chloride are formed. The latter sometimes combines with the excess of oxide, forming mercuric oxychloride.

Combinations.—1. With Ammonia.—Thénard's *fulminating mercury*, see MERCURY-BASES, AMMONIACAL, p. 918.

2. With Lime.—This compound is obtained, according to Berthollet, by boiling mercuric oxide with lime and water, separating the solution from the undissolved portion, and evaporating the liquid to the crystallising point. It then separates in yellow transparent crystals.

3. Mercuric Salts.—These salts are formed by dissolving mercuric oxide in acids; also by the action of oxidising acids aided by heat on metallic mercury; also with evolution of ammonia, on boiling various ammonium-salts with mercuric oxide. The normal salts may be represented by the formula Hg^nA_n, or $Hhg^nA_n{}^2$, the radicle Hg (= 100) being monatomic, and Hhg diatomic, in these salts, *e.g.*:

Mercuric nitrate . . $HgNO^3$ or $Hhg''(NO^3)^2 = \left.\begin{matrix}(NO^2)^2\\ Hhg^2\end{matrix}\right\}O^2$

Mercuric sulphate . . $\overset{''}{Hg}{}^2(SO^4)''$ or $Hhg''(SO^4)'' = \left.\begin{matrix}(SO^2)''\\ Hhg''\end{matrix}\right\}O^2$

Mercuric phosphate . . $Hg^3(PO^4)''' = \overset{''}{Hhg}{}^3(\overset{'''}{PO}{}^4)^2 = \left.\begin{matrix}(\overset{'''}{PO})^2\\ \overset{''}{Hhg}{}^3\end{matrix}\right\}O^6.$

The basic salts may be represented by formulæ similar to those of the basic mercurous salts, *e.g.*;

$$2Hhg''O.N^2O^5 = Hhg''O.Hhg''(NO^3)^2 = \overset{''}{Hhg}{}^2\left\{\begin{matrix}(NO^3)^2\\ O\end{matrix}\right. = \left.\begin{matrix}NO^2)^2\\ \overset{''}{Hhg}{}^2\end{matrix}\right\}O^2.$$

$$3Hhg''O.N^2O^5 = 2Hhg''O.Hhg'')NO^3)^2 = \overset{''}{Hhg}{}^3\left\{\begin{matrix}(NO^3)^2\\ O^2\end{matrix}\right. = \left.\begin{matrix}\overset{''}{Hhg}{}^3\\ (NO^2)^2\end{matrix}\right\}O^4$$

$$3Hhg''O.SO^3 = 2Hhg''O.Hhg'(SO^4)'' = \overset{''}{Hhg}{}^3\left\{\begin{matrix}(SO^4)''\\ O^2\end{matrix}\right. = \left.\begin{matrix}\overset{''}{Hhg}{}^3\\ (SO^2)''\end{matrix}\right\}O^4.$$

Normal mercuric salts are, for the most part, colourless; the basic salts yellow: they have a nauseous metallic taste, and are violent acrid poisons. They are decomposed by water, especially at the boiling heat, with separation, generally of a basic salt, but sometimes of mercuric oxide, as from the nitrate, the solution retaining sometimes an acid mercuric salt, sometimes a free acid. Hence H. Rose (Pogg. Ann. cvii. 298), regards mercuric oxide as the weakest of all basic oxides, no other oxide being precipitated from the solutions of its salts by water. In the solution of mercuric chloride, water forms no precipitate, either of oxide or basic salt, the oxide being precipitated from this solution only by strong bases, since mercury, like the other noble metals, has a stronger affinity for chlorine than for oxygen. Conversely, mercuric oxide precipitates strong bases from the solutions of their chlorides, but not of their oxygen-salts. Those oxides which, when added to a solution of mercuric chloride, do not form a precipitate either of oxide or oxychloride, are thrown down by mercuric oxide from their solutions in hydrochloric acid; whereas those which precipitate mercuric oxide from the solution of the chloride, are not thrown down by that oxide from the solutions of their own chlorides. Thus the *alkaline earths* are not precipitated from their solutions in hydrochloric acid by mercuric oxide. From solution of *manganous chloride*, the manganese is completely precipitated after some time, as manganous oxide (manganous sulphate, on the other hand, is not decomposed). From solution of *chloride of lead*, mercuric oxide throws down oxide of lead; from *chloride of zinc*, the red-brown oxychloride (sulphate and acetate of zinc are not decomposed by it). From the *chlorides of nickel* and *cobalt* it precipitates the protoxides of those metals, the former completely, the latter for the most part (the sulphates are not decomposed). From *ferrous chloride*, ferrous oxide is precipitated, the mercuric oxide immediately turning black, but becoming red again after a while; the liquid contains mercuric chloride, if the quantity of mercuric oxide present is not sufficient to form an oxychloride; and the insoluble residue consists of mercurous chloride and a ferric oxychloride, produced by the reaction, $Hhg''O + Ffe''Cl^2 = Hhg''Cl + Ffe'''OCl$. From *ferric chloride*, mercuric oxide in excess throws down all the iron as ferric oxide, forming an insoluble mercuric oxychloride (ammonio-ferric sulphate is not altered by it). From *cupric chloride* it throws down all the copper as cupric oxide; cupric sulphate is decomposed by it after a long time only, the mercuric oxide being converted at the same time into a solid lump of basic mercuric sulphate and basic cupric sulphate. (H. Rose.)

MERCURY, OXYBROMIDE OF. *Basic mercuric bromide.* $\overset{\prime\prime}{\text{Hg}}{}^4\text{Br}^2\text{O}^3$ or $3\text{Hg}''\text{O}.\text{Hg}''\text{Br}^2$.—This compound is obtained, according to Löwig, by boiling mercuric oxide and bromide together in water, or by boiling a solution of the bromide with a quantity of potash not sufficient to precipitate it completely. As thus prepared, it is a yellow crystalline powder, and crystallises from its aqueous solution in yellow needles. Rammelsberg obtained it, as a dark-brown powder, by precipitating mercuric bromide with carbonate of sodium.—Mercuric oxybromide is insoluble in cold, somewhat soluble in hot *water*, easily soluble in *absolute alcohol* (Löwig), insoluble in aqueous alcohol (Rammelsberg). It is resolved at a gentle heat into oxygen gas, a sublimate of mercury, mercurous and mercuric bromide, and a residue of mercuric oxide (Löwig). By boiling *potash*, it is converted, according to Löwig, into pure mercuric oxide; whereas, according to Rammelsberg, it remains unaltered. *Nitric acid* dissolves mercuric oxide from it, and leaves the bromide. (Rammelsberg.)

MERCURY, OXYCHLORIDE OF. Mercuric chloride and oxide unite in several proportions, and the compounds may be obtained in various ways: as by the action of mercuric oxide on a solution of the chloride; by incomplete precipitation of the latter solution with caustic alkalis or alkaline carbonates; and finally, by the action of chlorine on mercuric oxide. According to Millon, 1 at. mercuric chloride unites with 2, 3, or 4 at. mercuric oxide; but it is difficult to avoid obtaining mixtures of these several compounds. The usual mode of preparing them is to mix a solution of mercuric chloride saturated at 15°, with a solution of perfectly pure monopotassic carbonate (KHCO^3) saturated at the same temperature. A precipitate of pure oxychloride is then at once obtained; whereas if a neutral alkaline carbonate be used, the oxide is precipitated.

a. $\overset{\prime\prime}{\text{Hg}}{}^3\text{Cl}^2\text{O}^2 = \text{Hg}''\text{Cl}^2.2\text{Hg}''\text{O}$, is obtained by mixing 1 pt. of the solution of monopotassic carbonate with 6 to 10 pts. of the solution of mercuric chloride, stirring and immediately collecting the precipitate in a filter. It is a brick-red non-crystalline powder containing yellow mercuric oxide, which may be separated from it by potash. When 1 pt. of the solution of the acid potassium-salt is mixed with 3 or 4 pts. of the mercuric solution, the liquid being well stirred and then left to itself, a bright yellow precipitate is first formed, which gradually turns red, especially on agitation, afterwards acquires a tinge of purple-red, and ultimately of violet. It has exactly the same composition as the preceding. When 1 pt. of the potassic solution is mixed with 3 pts. of the mercuric solution, and the liquid is briskly stirred with a glass rod, black streaks begin to form on the side of the vessel; and if the contents are poured out, and a fresh mixture prepared, and briskly stirred, a dark precipitate is formed, the colour of which gradually passes into shining black. It has the same composition as the preceding; but when treated with potash, it yields red mercuric oxide.

β. $\overset{\prime\prime}{\text{Hg}}{}^4\text{Cl}^2\text{O}^3 = \text{HgCl}^2.3\text{Hg}''\text{O}$. Obtained on mixing the solutions in equal volumes, and leaving the mixture at rest. The liquid then becomes filled after a while with shining, golden-yellow, crystalline scales, from which potash separates yellow mercuric oxide.

γ. $\overset{\prime\prime}{\text{Hg}}{}^5\text{Cl}^2\text{O}^4 = \overset{\prime\prime}{\text{Hg}}\text{Cl}^2.4\text{Hg}''\text{O}$.—When 4 to 6 pts. of the potassic solution are mixed with 1 pt. of the mercuric solution, no precipitate is formed at first; but, after a while, carbonic anhydride is given off, and a brown crystalline crust, having the composition above given, forms on the surface of the liquid. The same compound is gradually deposited from all the liquids filtered from the preceding oxychlorides, and is likewise obtained by imperfect precipitation of a warm solution of mercuric chloride. Potash separates the red oxide from it. All the other oxychlorides are converted into this compound when treated with boiling water, the liquid then depositing, on cooling, shining crystalline scales, also consisting of the same compound, but containing the yellow modification of the oxide. The same compound is obtained, according to Thaulow, when chlorine gas is passed into water in which mercuric oxide is suspended; the analysis of the compound thus produced does not, however, quite agree with the formula of the tetrabasic chloride. (*Handwörterbuch der Chemie*, vi. 772.)

When a solution of mercuric chloride is boiled with mercuric oxide, or triturated with it, and then left to itself for a considerable time, several oxychlorides appear to be formed. A solution of mercuric chloride boiled with the oxide deposits, on cooling, a mixture of the several oxychlorides; and on decanting the liquid, as soon as it has cooled to 60°, it yields small rhombic crystals of the compound $\text{Hg}^3\text{Cl}^4\text{O}$ or $2\text{HgCl}^2.\text{HgO}$, which may be freed from admixed mercuric chloride by absolute alcohol. (Roucher.)

According to Roucher's latest experiments (Ann. Chim. Phys. [3] xxvii. 353; Jahresb. 1849, p. 283), the composition of the oxychloride formed by the action of mercuric chloride on mercuric oxide, is different, according as the red or the yellow modification of the oxide is used in its preparation, and likewise varies with the temperature and the nature of the solvent. At high temperatures, whether the red or yellow variety of the oxide be employed, and whether the chloride be used in the state of aqueous or of alcoholic solution, the products formedare invariably the same, viz., a black insoluble compound, $\mathrm{HhgCl^2.2HhgO}$, containing the red oxide, and a white, somewhat soluble substance, consistingof $\mathrm{2HhgCl^2.HhgO}$. At ordinary temperatures, the yellow oxide always produces the yellow compound $\mathrm{HhgCl^2.3HhgO}$. The red oxide, digested in the cold with excess of corrosive sublimate, dissolved either in water or in alcohol, forms black $\mathrm{HhgCl^2.2HhgO}$; but when the oxide is in excess, and the chloride is used in the state of aqueous solution and frequently renewed, a more energetic action takes place, and the compound formed is $\mathrm{HhgCl^2.6HhgO.H^2O}$; by operating in a similar manner, but using a somewhat larger quantity of the chloride solution at first, the anhydrous compound $\mathrm{HhgCl^2.6HhgO}$ is produced. Finally, the nature of the product is influenced by trituration: for, by triturating the red oxide in the cold with solution of corrosive sublimate renewed at short intervals, the product $\mathrm{HhgCl^2.4HhgO}$ is obtained.

All the mercuric oxychlorides yield, when heated, a sublimate of mercuric chloride, or are further decomposed into oxygen, mercurous and mercuric chlorides, and a residue of mercuric oxide.

MERCURY, OXYCYANIDE OF. See CYANIDES (ii. 255).

MERCURY, OXYFLUORIDE OF. See p. 903.

MERCURY, OXYGEN-SALTS OF. For the general characters of these salts, see pp. 899, 900; and for the special descriptions, see the several Acids.

MERCURY, OXY-IODIDE OF. *Basic mercuric iodide.* $\mathrm{\overset{''}{Hhg}{}^4I^2O^3 = HhgI^2.3HhgO}$.—This compound is obtained by melting the oxide and iodide together in the required proportions, or by heating the iodide with dilute potash-ley. It is a yellowish-brown powder, mostly mixed with excess of oxide. [For its reactions with ammonia, see MERCURY-BASES, AMMONIACAL, p. 919].

MERCURY, PHOSPHIDE OF. This compound is formed:—1. By heating finely-divided mercury with 1½ pt. phosphorus (Pelletier); 2. By digesting 2 pts. of mercuric oxide with 1½ phosphorus and 1 water, mercuric phosphate being formed at the same time (Pelletier); 3. By decomposing heated calomel with vapour of phosphorus (H. Davy); 4. By boiling aqueous mercuric chloride with phosphorus (Boullay); 5. In the decomposition of aqueous mercurous nitrate by phosphoretted hydrogen gas (Thomson); 6. When phosphoretted hydrogen gas is passed over dry, slightly-heated mercuric chloride, whereupon the phosphide of mercury sublimes. (H. Rose.)

Phosphide of mercury (1 and 2) is black; may be cut with a knife; gives off, when distilled, first the phosphorus, and afterwards the mercury; and, when exposed to the air, gradually loses its phosphorus by oxidation. That prepared by method (3) is brown (H. Davy), brown-red (Berzelius); according to Davy, it remains solid at the boiling point of mercury, and may be preserved unaltered. That prepared by (5) has the form of dark-brown flakes. The preparation (6) is an orange-yellow sublimate, which, when somewhat suddenly heated, is resolved into phosphorus and mercury. (H. Rose, Pogg. Ann. xxiv. 335.)

MERCURY, PHOSPHOCHLORIDES OF.—*a.* $\mathrm{\overset{''}{Hhg}{}^6P^2Cl^6.3H^2O = \overset{''}{Hhg}{}^3P^2.3Hhg''Cl^2.3H^2O}$.—Formed by passing phosphoretted hydrogen-gas through an aqueous or alcoholic solution of mercuric chloride. It is a yellow powder, which, when *heated* in a retort, yields a large quantity of hydrochloric acid-gas, 77·59 per cent. metallic mercury, and a residue of phosphoric acid. By boiling with *water*, it yields metallic mercury and a solution of hydrochloric and phosphorous acids free from mercury. *Caustic potash* decomposes it in a similar manner. Heated with dilute *nitric acid*, it eliminates nitric oxide, and is converted into 86·77 per cent. of calomel. (H. Rose, Pogg. Ann. xl. 75.)

β. $\mathrm{Hhg^3P^2Cl^{16} = 3HhgCl^2.2PCl^5}$.—Obtained by direct combination of pentachloride of phosphorus with mercuric chloride. It forms easily-fusible needles, which volatilise at about 200°, and decompose when suddenly heated. (Baudrimont, Compt. rend. lv. 361.)

MERCURY, SELENIDE OF. *Mercuric Selenide*, $\mathrm{Hhg''Se}$, may be produced artificially by direct union of its elements at a high temperature. As thus prepared, it forms a tin-white mass, which, when strongly heated, sublimes without previous fusion in grey metallic-shining laminæ. It obstinately resists the action of the greater number of solvents, but is dissolved by *nitromuriatic acid*, as mercuric selenite. *Nitric acid* produces the same oxidation, but only after long-continued boiling.

Selenides of mercury occur at *Zorge* and at Tilkerode in the Harz, and near Clausthal. Their composition is exhibited in the following table:

	Tilkerode. Schulz.	*Zorge.* Marx.	*Clausthal.* Kerl.	
Mercury . .	74·02	74·5	75·11	74·82
Selenium . .	23·61	25·5	24·39	24·90
Sulphur . .	0·70			
	98·33	100·0	99·50	99·72

The Tilkerode mineral contains also a trace of copper. When it is heated before the blowpipe, the greater part volatilises, leaving 11·85 per cent. of foreign matter, including 10·85 per cent. ferric oxide). The preceding analysis applies to the volatile portion. If the loss be reckoned as selenium, the mineral has very nearly the composition Hg^2Se or $Hh''gSe$. The analyses of the minerals from Zorge and Clausthal lead nearly to the formula Hhg^4Se^5, which is that of a mercuroso-mercuric selenide containing $\acute{H}hg^2Se.4Hhg''Se$. It is possible however that these minerals may really consist also of mercuric selenide $Hhg''Se$ (Rammelsberg's *Mineralchemie*, pp. 35, 1010).

The native selenides of mercury are massive minerals, with compact granular texture and no cleavage. Hardness = 2·5. Specific gravity = 7·1 to 7·37 (of the Clausthal ore). Lustre metallic. Streak shining. Colour steel to blackish lead-grey.

Selenide of Mercury and Lead forms the mineral *Lehrbachite*, occurring at Tilkerode (pp. 558, 570).

Selenide of Mercury, Lead, and Copper.—Minerals having this composition occur at Tilkerode and at Zorge in the Harz; they are intimate mixtures, in which a white or grey mineral crystallised in small cubes, and a violet mineral, may be distinguished. Two specimens analysed in Rammelsberg's laboratory gave

	Se.	Pb.	Cu.	Hg.		
a. (Specific gravity 5·74)	38·53	25·36	22·13	13·12	=	99·14
b. („ „ 4·86)	34·19	43·05	17·49	3·61	=	98·34

MERCURY, SELENIO-SULPHIDE OF. *Onofrite.*—A mineral occurring with other ores of mercury near San Onofre in Mexico. It contains according to H. Rose's analysis (Pogg. Ann. xlvi. 315), 6·49 per cent. selenium, 10·30 sulphur, and 81·33 mercury; whence it appears to be a compound, or perhaps an isomorphous mixture, of 1 at. $HhgSe$ and 4 at. $HhgS$. In its physical characters it resembles mercuric selenide.

Del Rio (Pogg. Ann. xiv. 182) mentioned a grey mineral from Calabras in Mexico containing 49 per cent. selenium, 1·5 sulphur, 24 zinc, and 19 mercury; also a red mineral likewise containing selenium, mercury, and zinc. Subsequently (*ibid.* xxxix. 526), he described the latter as a mixture of selenio-sulphide of mercury, selenide of cadmium, selenide of iron, and free selenium.

MERCURY, SULPHIDES OF. Mercury forms two sulphides, analogous to the oxides.

Mercurous Sulphide. Hg^4S or Hhg^2S. This is the black precipitate formed by sulphydric acid or sulphide of ammonium in solutions of mercurous salts. It may be prepared by passing sulphydric acid gas through a solution of mercurous acetate; if the nitrate is used, the liberated nitric acid exerts an oxidising action on the precipitate. The best mode of preparation, according to Berzelius, is to drop a dilute solution of mercurous nitrate into a dilute solution of sulphydrate of ammonium or potassium; or a solution of either of these sulphydrates may be poured upon calomel recently precipitated and still moist.

Mercurous sulphide in the dry state is a deep-black powder; it is resolved at a gentle heat into mercuric sulphide and metallic mercury, which remains mixed with the sulphide in the form of small globules. At a stronger heat, it yields a sublimate, first of metallic mercury, afterwards of cinnabar.

Mercuric Sulphide. Hg^2S or $Hhg''S$. This compound exists both amorphous and crystallised; in the former state it is black; in the latter, it has a fine red colour and constitutes the well-known pigment called cinnabar or vermillion.

a. Amorphous Mercuric Sulphide.—When mercury and sulphur are triturated together for a long time in the proportion 100 mercury to 16 sulphur, they unite and form black mercuric sulphide; the product thus obtained is called in pharmacy, *Aethiops mineralis.*—The same compound is formed by heating 6 pts. mercury with 1 pt. sulphur; but the product thus obtained is of rather uncertain composition, owing to the volatilisation of a portion of the sulphur; moreover it contains a considerable quantity of cinnabar, which remains undissolved on boiling with potash, whereas good *Aethiops* is wholly or almost wholly soluble in that liquid.—The amorphous sulphide is also produced by precipitating the solution of a mercuric salt with excess of sulphydric acid or a soluble sulphide; by agitating mercury with pentasulphide of ammonium or potassium; and by exposing cinnabar to a very gentle heat in a close vessel.

Amorphous mercuric sulphide is a velvet-black powder or a greyish-black mass When heated somewhat strongly in a close vessel, it yields a sublimate of cinnabar; but on heating it in contact with the *air*, the sulphur burns and the mercury volatilises; when ignited with *caustic alkalis* or *alkaline carbonates*, it gives off all its mercury and leaves a residue of alkaline sulphide (liver of sulphur). It withstands the action of most solvents, but is decomposed, with separation of sulphur, by very strong *nitric acid;* dilute nitric acid has scarcely any action upon it; *nitromuriatic* acid dissolves it with tolerable facility. It is likewise soluble in aqueous *sulphide of potassium*, and the solution solidifies on evaporation to a mass of slender colourless needles consisting of potassio-mercuric sulphide, $K^2Hhg''S^2.5H^2O$, which is decomposed by water, with separation of black mercuric sulphide.

β. *Crystallised mercuric sulphide*. *Cinnabar*, *Vermillion*. Cinnabar occurs native, being in fact the most important ore of mercury: its principal localities have been already enumerated (p. 883). By far the greater part of the vermillion occurring in commerce is however prepared by sublimation of the amorphous sulphide.

Formation and preparation.—1. *In the dry way.*—Mercury, mercuric oxide, or trimercuric sulphate, sublimed with sulphur, yields cinnabar. When 5 or 6 parts of mercury are added to 1 part of melting sulphur, and the mixture is heated, with constant stirring, till the sulphur becomes thick, combination takes place suddenly, attended with evolution of light and heat, and with violent crackling and projection of the mass. The resulting compound exhibits a blackish-red colour, and frequently a distinct red streak; it may be regarded as cinnabar partly mixed with black sulphide of mercury, and partly with uncombined mercury and sulphur in a state of minute division. Now, when this crude product, after being pounded, is mixed with a small quantity of sulphur, and a glass flask half filled with it is loosely closed with a charcoal stopper, sunk to two-thirds of its depth in sand, and exposed for some hours to a red heat in a slow-drawing wind-furnace, a sublimate of pure cinnabar is obtained. The excess of sulphur, being more volatile than the cinnabar, escapes; foreign metals remain in the form of sulphides at the bottom of the flask. If the upper part of the flask becomes too hot, a portion of the cinnabar may be lost by volatilisation.

Old method of preparation in Amsterdam.—170 pounds of mercury are gradually added to 50 pounds of melted sulphur contained in a cast-iron pot, the materials being stirred up with an iron spatula, but not so rapidly as to give rise to active combustion —the mixture is poured out upon an iron plate, and broken into pieces after cooling— and the fragments are put into hand-jars capable of holding 1½ pounds of water. The subliming vessels are earthern cylinders 4 feet high, glazed within, and closed at the bottom; they are sunk to two-thirds of their depth in a furnace in which their lower part is heated to redness. A few hand-jars full of the mixture are thrown into each of these subliming vessels, and the contents left to crackle and burn till the greater part of the excess of sulphur volatilises, and the flame diminishes. The smooth, level opening is then covered with a thick, smooth plate of cast-iron; the plate removed as soon as a sufficient quantity of cinnabar has collected upon it; the cinnabar which has collected on the upper part of the vessel is pushed down again; a fresh plate put on, &c. &c. The contents of the cylinder are stirred up from time to time, and fresh material is introduced. The cinnabar, after being detached from the plates, is ground as finely as possible with rain-water.

Method of preparation in Idria.—A number of casks, each containing 8 pounds of ground sulphur and 42 pounds of mercury, are made to turn upon their axes for two or three hours, till the contents are converted, with slight evolution of heat, into a brown powder. 100 pounds of this powder are then introduced into an upright cast-iron cylinder, previously heated in a furnace; the cylinder is covered with an iron capital, kept down by weights till the crackling of the mass is over; and the iron capital is then replaced by one of stone-ware, having its beak connected with a tube and receiver, and the fire is increased. The best cinnabar collects in the capital, which is afterwards broken in pieces; that which condenses in the tube and receiver, if mixed with excess of sulphur, is added to the quantity introduced at the next sublimation. The cinnabar, after being finely ground with water, is well boiled with potash-ley, and washed with boiling and with cold water. (Mitscherlich, *Lehrbuch.*)

Chinese method.—1 part of sulphur and 4 parts of mercury are sublimed in an earthen vessel, to which an iron cover, kept constantly moist, is luted; the fire is kept up for four-and-twenty hours; the vessel broken up after cooling; the less pure sublimate separated; the purer portion pounded up; the powder sifted into a large vessel filled with water; the water, with the scum floating on it, is poured off after a while, the process being twice repeated; and lastly, the sediment at the bottom is dried. (*N. Edinb. J. of Sc.* ii. 352.)

European cinnabar, whether prepared in the dry or in the wet way, always has a tinge of yellow; the Chinese, which is six times as dear, inclines to carmine colour, although no foreign matter can be detected in it, excepting a little glue. By the sublimation of common cinnabar with 1 per cent. of sulphide of antimony, a dark steel-grey cinnabar is obtained, which becomes brown-red when pulverised: but if it be finely ground, and repeatedly boiled with solution of liver of sulphur, then thoroughly washed and digested with hydrochloric acid, and afterwards washed and dried, it becomes exactly like the Chinese vermillion, but of a still finer colour. No antimony can be detected in it. (Wehrle, *Zeitschr. phys. v. Wiss.* ii. 27.)

The principal point to be attended to in the preparation of cinnabar by sublimation, is that no black amorphous sulphide shall get mixed with it.

2. *In the wet way.*—The black, amorphous sulphide of mercury obtained by the action of sulphydric acid, or of alkaline sulphydrates or persulphides on mercury, its oxides, and salts, is converted by contact with alkaline persulphides, slowly in the cold, but quickly when heated, into the red sulphide.

Very fine cinnabar may be obtained by immersing recently precipitated "white precipitate" (p. 916) in a solution of sulphydrate of ammonium, or in monosulphide of ammonium previously saturated with sulphur: the black colour which the precipitate first acquires passes, at a temperature between 40° and 50°, through red-brown into the beautiful deep red of Chinese vermillion, the change taking place more quickly as the liquid is more concentrated. The colour may be rendered still brighter by subsequent digestion with potash at a gentle heat. (Liebig, Ann. Ch. Pharm. v. 289; vii. 49.)

Brunner (Pogg. Ann. xv. 593) carefully triturates 100 pts. of mercury with 38 pts. of flowers of sulphur, till the whole is converted into black amorphous sulphide—a process which requires three hours for small quantities, and twelve hours if the quantity amounts to a few pounds—and heats it in a porcelain basin or a cast-iron pot, with a solution of 25 pts. of potassium-hydrate in 133 to 150 pts. of water, keeping the temperature uniformly at 45°, and never letting it rise above 50°. At first the mixture is continually stirred with the pestle, afterwards from time to time. The water which evaporates is replaced, so as not to allow the mixture to acquire the thickness of a jelly. When the reddening has once begun, which generally takes place in about eight hours, the heat must not be allowed to rise above 45°; and as soon as the red has attained its greatest degree of brightness, the vessel is removed from the fire, or else, which is better, the mixture is kept for some hours exposed to a gentler heat. It is then washed, and the mercury which remains metallic is separated by levigation, whereupon it yields from 109 to 110 per cent. of cinnabar, but little inferior to the finest native variety, and far superior to that obtained by sublimation. The above-mentioned proportion of the ingredients gives the largest amount of cinnabar; 100 pts. of mercury yield with 40 pts. of sulphur and 40 of potassium-hydrate, 107 cinnabar; with 28·3 sulphur and 51 potassium-hydrate, 94·2; with 33 to 40 sulphur and 60 potassium-hydrate, 81·5; and with 30 sulphur and 60 potassium-hydrate, only 47·3 cinnabar. (Brunner.)

Döbereiner (Schw. J. lxi. 380) gently heats mercury with a solution of pentasulphide of potassium, triturating it continually, till the mercury is converted into a dark red powder, a change which generally takes place in about an hour and a half; he then decants the liquid (which contains protosulphide of potassium, and by digestion with sulphur may be rendered fit for another preparation of cinnabar), and triturates the powder with a small quantity of dilute potash-ley at 40° or 45°, till it acquires a fiery red colour.

If the cinnabar has become brown from being heated too long with sulphur and potash-ley, it may be restored to the state of the finest vermillion by the addition of water and the application of a moderate heat. (Storch, Repert. Pharm. xxxv. 107.)

Th. Martius (Kastn. Arch. x. 497) places the ingredients in bottles closed with corks and packs them into a box, which is fastened to the upper beam of a saw-mill. In 24 or 36 hours, at ordinary temperatures, the most beautiful cinnabar is obtained; it is afterwards washed and dried. This method not only has the advantage of dispensing with the labour of trituration, but likewise prevents the hitherto unexplained passage of the cinnabar into the brown state, which is so liable to take place on the application of heat.

Adulterations.—*Brickdust* remains behind on ignition.—*Oxide of iron*, the same; it may also be dissolved out by hydrochloric acid.—*Red lead* remains behind on ignition in the form of a fused protoxide, and yields chloride of lead, with evolution of chlorine, on boiling the substance with hydrochloric acid; the chloride thus formed may be extracted by boiling water.—*Dragon's Blood:* Empyreumatic odour on the application of heat; gives a red colour to alcohol.

Properties.—Native cinnabar and many of the artificial varieties form hemihedral crystals belonging to the hexagonal system, the primary form being an acute rhombohedron, in which the length of the principal axis is 2·29, and R : R in the terminal edges 71° 48′. The most ordinary combination is R . oR, somewhat like *fig.* 361 (ii. 224); also with ∞R, the latter sometimes predominating. Cleavage parallel to ∞R. Cinnabar obtained by sublimation assumes the form of fibrous masses. Specific gravity of the native mineral, 8·0 to 8·1; of a cleavable variety from Neumarktel, 8·998; of the artificially sublimed compound, 8·0602 (Karsten), 8·124 (Pol. Boullay). Hardness of the native mineral = 2 to 2·5. It is sectile and has a subconchoidal uneven fracture. In the mass it is cochineal-coloured, transparent, and has an adamantine lustre; its powder is scarlet. It becomes brownish when gently heated; quite brown at 250°, and black at a higher temperature; but if the heat has not been strong enough to cause it to volatilise, it recovers its fine scarlet colour on cooling.

Pure mercuric sulphide contains 86·2 per cent. mercury and 13·2 sulphur; native cinnabar is, for the most part, nearly pure, the percentage of mercury varying from about 78 to 86 per cent.

In its chemical relations cinnabar, both natural and artificial, resembles the amorphous sulphide, excepting that it is still less easily attacked by solvents. Heated with *iron*, *tin*, *antimony*, and several other metals, it yields metallic mercury and a sulphide of the other metal. *Caustic alkalis* and *alkaline carbonates* also liberate the mercury at a red heat, while a mixture of metallic sulphide and sulphate remains behind; thus with *lime:*

$$4\mathrm{HhgS} + 4\mathrm{CcaO} = \mathrm{Hhg}^4 + 3\mathrm{CcaS} + \mathrm{CcaSO}^4.$$

Heated with *protoxide of lead*, it gives off sulphurous anhydride and mercury, leaving very pure metallic lead, and a fused slag, which, if the oxide of lead is not in very great excess, contains undecomposed cinnabar.

MERCURY, SULPHOBROMIDE OF. $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^3\mathrm{Br}^2\mathrm{S}^2$, $\mathrm{HhgBr}^2.2\mathrm{HhgS}$. When sulphydric acid gas is passed through a solution of mercuric bromide, a white precipitate is at first formed, consisting of this compound, which is afterwards transformed by excess of sulphydric acid into black mercuric sulphide. The sulphobromide is also produced by digesting the black sulphide with the aqueous solution of the bromide. It is yellowish-white when dry; splits up into mercuric bromide and cinnabar when heated; is blackened by alkalis, but less quickly than the corresponding chlorine-compound. It is neither decomposed nor dissolved by nitric or sulphuric acid at the boiling heat.

MERCURY, SULPHOCHLORIDE OF. $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^3\mathrm{Cl}^2\mathrm{S}^2$. Produced by reactions similar to those above described, for the sulphobromide which it resembles in its properties and in most of its reactions. Heated in a current of chlorine gas, it yields chloride of sulphur and mercuric chloride.

MERCURY, SULPHO-IODIDE OF. $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^2\mathrm{I}^2\mathrm{S} = \mathrm{H}\overset{\prime\prime}{\mathrm{h}}\mathrm{gI}^2.\mathrm{H}\overset{\prime\prime}{\mathrm{h}}\mathrm{gS}$. Produced like the preceding compound, which it resembles.

MERCURY-BASES, AMMONIACAL. (C. G. Mitscherlich, Pogg. Ann. ix. 387; xvi. 41.—Kane, Ann. Ch. Phys. [2] lxxii. 215.—Plantamour, Ann. Ch. Pharm. xl. 115.—Rammelsberg, Pogg. Ann. lv. 248.—Millon, Ann. Ch. Phys. [3] xviii. 333.—Hirzel, *Ueber die Einwirkung des Quicksilberoxyds auf das Ammoniak und die Ammoniak-verbindungen*, Leipzig, 1852; *abstr.* Ann. Ch. Pharm. lxxxiv. 258.—Schmieder, J. pr. Chem. lxxv. 129; Jahresb. 1858, p. 204.)—By the action of ammonia and its salts on mercury-compounds, a variety of substances are formed, some of which were originally regarded as compounds of ammonia with mercury-salts; *e.g.*, *ammonio-mercuric chloride* $\mathrm{NH}^3.\mathrm{Hhg}''\mathrm{Cl}^2$; *ammonio-mercurous chloride*, $\mathrm{NH}^3.\mathrm{Hhg}'\mathrm{Cl}$; *ammonio-mercuric iodide*, $2\mathrm{NH}^3.\mathrm{Hhg}''\mathrm{I}^2$, &c. Kane, in accordance with his amidogen theory, regarded these compounds as containing *amide of mercury*, $\mathrm{NH}^2\mathrm{Hg}$, combined with other mercury- or amidogen-compounds. Hirzel and others have represented them as containing *nitride of mercury*, NHg^3, as a proximate constituent. Gerhardt first suggested that they contain ammonia-molecules, in which the hydrogen is more or less replaced by mercury; and this view has been further developed, in accordance with the ammonium-theory, these compounds being supposed to contain ammonium-molecules, in which the hydrogen is wholly or partly replaced by mercury in the proportion of 100 or 200 pts. mercury to 1 pt. hydrogen, according as the compound is formed from a mercuric or a mercurous salt, thus:

Mercurammonium	$\mathrm{NH}^3\mathrm{Hg}$ or $\mathrm{N}^2\mathrm{H}^6\mathrm{Hhg}''$
Mercurosammonium	$\mathrm{NH}^3(\mathrm{Hg}^2)'$ or $\mathrm{NH}^3\mathrm{Hhg}'$
Dimercurammonium	$\mathrm{NH}^2\mathrm{Hg}^2$ or $\mathrm{N}^2\mathrm{H}^4\mathrm{H}\overset{\prime\prime}{\mathrm{h}}\mathrm{g}^2$

Dimercurosammonium	$\mathrm{NH^2(Hg^4)''}$ or $\mathrm{NH^2\overset{\prime}{H}hg^2}$
Trimercurammonium	$\mathrm{NHHg^3}$ or $\mathrm{N^2H^2\overset{\prime}{H}hg^3}$
Trimercurosammonium	$\mathrm{NH(Hg^6)'''}$ or $\mathrm{NH\overset{\prime}{H}hg^3}$
Tetramercurammonium	$\mathrm{NHg^4}$ or $\mathrm{N^2\overset{\prime\prime}{H}hg^4}$

None of the mercurammoniums have been obtained in the free state; but trimercuramine, $\mathrm{Hg^3N}$ or $\mathrm{\overset{\prime\prime}{H}hg^3N^2}$, is produced by the action of ammonia-gas on dry mercuric oxide.

Mercurammonium. $\left.\begin{matrix}\mathrm{Hg}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{N}$ or $\left.\begin{matrix}\mathrm{Hhg''}\\ \mathrm{H^6}\end{matrix}\right\}\mathrm{N^2}$—The *bromide* of this base, $\left.\begin{matrix}\mathrm{Hg}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{NBr}$ or $\left.\begin{matrix}\mathrm{Hhg''}\\ \mathrm{H^6}\end{matrix}\right\}\mathrm{N^2Br^2}$, (like ϵ or η,* p. 921) is produced by melting mercuric bromide at a gentle heat in ammonia gas, the salt then taking up about 3·4 per cent. of the gas. Water extracts bromide of ammonium from the product, and leaves a yellow powder which gives off ammonia when treated with aqueous sulphide of potassium, but not with caustic potash.

Bromide of Mercury and Mercurammonium. $\mathrm{NH^3.2HgBr} = \left.\begin{matrix}\mathrm{Hg}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{NBr.HgBr} = \left.\begin{matrix}\mathrm{Hhg''}\\ \mathrm{H^6}\end{matrix}\right\}\mathrm{N^2Br^2}.\ \mathrm{HhgBr^2}$, or *Bromide of Hydrogen and Dimercurammonium* $\mathrm{NH^3.Hhg''Br^2} = \left.\begin{matrix}\mathrm{Hhg''}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{N.HBr}$, ($\beta$), is produced by saturating mercuric bromide with ammonia gas. It is a white powder insoluble in water and in alcohol, sparingly soluble in ammonia, and is resolved by heat into nitrogen, ammonia gas, aqueous vapour, [? hydrogen], and a sublimate of mercuric bromide.

Chloride of Mercurammonium.—$\mathrm{NH^3.HgCl} = \left.\begin{matrix}\mathrm{Hg}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{NCl}$ or $\left.\begin{matrix}\mathrm{Hg''}\\ \mathrm{H^6}\end{matrix}\right\}\mathrm{N^2Cl^2}$, ($\epsilon$). *Fusible white precipitate.* Obtained by precipitating a solution of ammonio-mercuric chloride (*alembroth salt*, p. 808) with potash (Wöhler), or by dropping a solution of mercuric chloride into a boiling solution of sal-ammoniac mixed with free ammonia, as long as the resulting precipitate redissolves; it then separates on cooling in garnet-dodecahedrons (Mitscherlich). At a gentle heat it gives off half its ammonia, leaving the compound $\mathrm{NH^6.Hhg''Cl^2}$, (λ), which is also formed by gently heating mercuric chloride in a stream of ammonia gas, or by distilling mercuric oxide with sal-ammonia. (Mitscherlich.)

Iodide.—$\mathrm{NH^3.HgI} = \left.\begin{matrix}\mathrm{Hg}\\ \mathrm{H^3}\end{matrix}\right\}\mathrm{NI}$ or $\left.\begin{matrix}\mathrm{Hhg''}\\ \mathrm{H^6}\end{matrix}\right\}\mathrm{N^2I^2}$, ($\eta$). Red mercuric iodide absorbs ammonia gas and forms this white compound, which however, when exposed to the air, gives off its ammonia and is reconverted into red mercuric iodide. (H. Rose.)

The compound $\mathrm{NH^3.Hhg''I^2}$ (δ) is obtained by drenching mercuric iodide with aqueous ammonia, as a white crystalline powder which dissolves in excess of ammonia, leaving a brown powder consisting of hydrated iodide of tetramercurammonium; on evaporating the ammonical solution, the compound is deposited in small crystals. It quickly gives off its ammonia when exposed to the air, and is likewise decomposed by water and by acids. (Caillot and Corriol; Rammelsberg.)

Dimercurammonium. $\left.\begin{matrix}\mathrm{Hg^2}\\ \mathrm{H^2}\end{matrix}\right\}\mathrm{N}$ or $\left.\begin{matrix}\mathrm{\overset{\prime\prime}{H}hg^2}\\ \mathrm{H^4}\end{matrix}\right\}\mathrm{N^2}$. The *chloride* of this base $\left.\begin{matrix}\mathrm{\overset{\prime\prime}{H}hg^2}\\ \mathrm{H^4}\end{matrix}\right\}\mathrm{N^2Cl^2}$ (α or ζ), known in pharmacy as infusible white precipitate, *Mercurius præcipitatus albus*, is formed by adding ammonia to a solution of mercuric chloride. When first produced it is bulky and milk-white, but by contact with hot water, or by much washing with cold water, it turns yellow and is converted into hydrated chloride of tetramercurammonium, $\mathrm{\overset{\prime\prime}{H}hg^4N^2Cl^2.2H^2O}$. It is readily dissolved by acids, and is especially distinguished from calomel by its behaviour with ammonia, which does not alter white precipitate, whereas calomel is blackened by it. Kane regards this compound as an *amidochloride of mercury*, $\mathrm{HgH^2N.HgCl}$.

The tetrammonium salts (p. 918), all of which contain water, may be regarded as compounds of dimercurammonium salts with mercuric oxide, *e. g.* the chloride $\mathrm{\overset{\prime\prime}{H}hg^4N^2Cl^2.2H^2O}$ or $\mathrm{\overset{\prime\prime}{H}hg^2H^4N^2Cl^2.2Hhg''O}$. In like manner, *ammoniacal turpethum*, the salt produced by the action of ammonia on mercuric sulphate, and described at p. 920 as a sulphate of tetramercurammonium, $\mathrm{(\overset{\prime\prime}{H}hg^4N^2)SO^4.2H^2O}$, may be regarded as a basic sulphate of dimercurammonium, $\mathrm{(\overset{\prime\prime}{H}hg^2H^4N^2)SO^4.2Hhg''O}$.

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* The Greek letters in this and the following paragraphs refer to the table on page 921.

A double *sulphate of ammonium and dimercurammonium* $\left.\begin{matrix}\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^2\mathrm{H}^4\mathrm{N}^2\\ 2\mathrm{H}^4\mathrm{N}\end{matrix}\right\}\mathrm{S}^2\mathrm{O}^8.2\mathrm{H}^2\mathrm{O}$, ($\nu$), is obtained by adding mercuric oxide by small portions to a cold saturated solution of sulphate of ammonium, waiting each time for the last portion to dissolve, till the liquid begins to show turbidity, from separation of a white basic compound. On leaving this solution to evaporate at ordinary temperatures (if evaporated over the water-bath, it again deposits a white basic compound), the double salt crystallises from it in small white needles, or more definite colourless rhombic crystals, which give off their water at 115°. The salt dissolves easily in sulphate or chloride of ammonium, also in hydrochloric acid, either dilute or concentrated, and in very dilute sulphuric or nitric acid, but is insoluble in strong nitric acid, and is completely decomposed by strong sulphuric acid at the boiling heat.

The double salt is completely decomposed by water, even in the cold, and converted into a heavy, white, earthy powder, consisting of the basic salt, $2(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^2\mathrm{H}^4\mathrm{N}^2)\mathrm{SO}^4.3\mathrm{Hhg}''\mathrm{O}$, ($\psi$), which likewise separates, when a solution of sulphate of ammonium, saturated with mercuric oxide, is poured into water. It resembles the sulphate of tetramercurammonium (*ammoniacal turpethum*) above mentioned. The latter is also produced by boiling the finely triturated double salt with water, continually renewed as long as it takes up any sulphuric acid.

Another basic compound is obtained by dissolving the above-described double salt in cold dilute sulphuric acid, and adding the solution to an excess of dilute potash-ley; ammonia is then given off, and a white substance separates, which, when washed with water, and dried at 115°, has the composition $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^2\mathrm{H}^4\mathrm{N}^2\mathrm{SO}^4.3\mathrm{Hhg}''\mathrm{O}$, or $(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2)\mathrm{SO}^4.\mathrm{Hhg}''\mathrm{O}.2\mathrm{H}^2\mathrm{O}$, ($\phi$).

The solution of the last described compound, or of the double salt, in hydrochloric acid, poured into cold dilute potash-ley, kept constantly in excess, forms a white precipitate of $(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^2\mathrm{H}^4\mathrm{N}^2)\mathrm{Cl}^2.3\mathrm{Hhg}''\mathrm{O}$ or $(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2)\mathrm{Cl}^2.\mathrm{Hhg}''\mathrm{O},2\mathrm{H}^2\mathrm{O}$, ($\beta'$). This compound dissolves in boiling aqueous chloride of ammonium, giving off ammonia, and forming a double chloride of ammonium and dimercurammonium, which however has not yet been obtained pure. Finally, by boiling the last-mentioned compound with strong potash-ley till its colour changes from white to yellow, another oxychloride is obtained, having the composition $(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^2\mathrm{H}^4\mathrm{N}^2)\mathrm{Cl}^2.4\overset{\prime\prime}{\mathrm{H}}\mathrm{hgO}$ or $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2\mathrm{Cl}^2.2\mathrm{Hhg}''\mathrm{O}.2\mathrm{H}^2\mathrm{O}$, ($\alpha'$), and by continued boiling for a day with fresh portions of potash-ley, more and more chlorine and nitrogen may be removed, till at last nothing is left but pure mercuric oxide. (Schmieder.)

Trimercuramine $\mathrm{Hg}^3\mathrm{N}$ or $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^3\mathrm{N}^2$. This compound is formed by passing dry ammonia gas over precipitated mercuric oxide previously well washed and dried:

$$3\mathrm{HhgO} + 2\mathrm{NH}^3 = \mathrm{Hhg}^3\mathrm{N}^2 + 3\mathrm{H}^2\mathrm{O}.$$

The excess of oxide being removed by nitric acid, the trimercuramine is obtained in the form of a dark flea-brown powder, which explodes by heat, friction, percussion, or contact with oil of vitriol, almost as violently as iodide of nitrogen. When cautiously heated with hydrate of potassium, it is decomposed without detonation, yielding ammonia-gas and sublimed mercury. It is also decomposed by hydrochloric, sulphuric and concentrated nitric acid, yielding an ammoniacal and a mercuric salt. (Plantamour, Ann. Ch. Pharm. xl. 115.)

By the action of various ammonia-salts at a boiling heat on mercuric oxide, compounds are obtained, which may be regarded as compounds of trimercuramine with mercuric salts: thus with phosphate of ammonium, the salt $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^3\mathrm{N}^2.\mathrm{Hhg}^3\mathrm{P}^2\mathrm{O}^8.2\mathrm{H}^2\mathrm{O}$ (μ); with the acetate, the compound $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^3\mathrm{N}^2.\mathrm{C}^4\mathrm{H}^6\mathrm{Hhg}''\mathrm{O}^4.4\mathrm{H}^2{}''\mathrm{O}$ (λ) (Hirzel). These compounds may also be regarded as salts of tetramercurammonium (p. 918).

Trimercurammonium. $\left.\begin{matrix}\mathrm{Hg}^3\\ \mathrm{H}\end{matrix}\right\}\mathrm{N}$ or $\left.\begin{matrix}\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^3\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{N}^2$. The only known salt of this base is the *nitrate*, $\left.\begin{matrix}\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^3\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{N}^2.(\mathrm{NO}^3)^2.2\mathrm{H}^2\mathrm{O}$, ($\rho$), which is produced as a white precipitate on mixing a dilute and very acid solution of mercuric nitrate with very dilute ammonia. It might also be regarded as a *basic nitrate of mercurammonium*, $\left.\begin{matrix}\mathrm{Hhg}''\\ \mathrm{H}^6\end{matrix}\right\}\mathrm{N}^2.(\mathrm{NO}^3)^2.2\mathrm{Hhg}''\mathrm{O}$, or according to Mitscherlich, as a *basic ammonio-nitrate of mercury*, $2\mathrm{NH}^3.3\mathrm{Hhg}''\mathrm{O}.\mathrm{N}^2\mathrm{O}^5$.

Tetramercurammonium, $\mathrm{Hg}^4\mathrm{N}$ or $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2$. By acting on mercuric oxide with aqueous ammonia, a brown compound is obtained, the so-called mercuramine, which may be regarded as a hydrated oxide of tetramercurammonium $\left.\begin{matrix}\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2.\mathrm{H}^2\mathrm{O}$. It is a strong base and forms definite salts, from which it is separated by acids, without decomposition, at ordinary temperatures. It may also be regarded as oxide of dimercurammonium combined with mercuric oxide, viz. as $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^2\mathrm{H}^4\mathrm{N}^2\mathrm{O}.2\mathrm{Hhg}''\mathrm{O}$, and its salts represented by corresponding formulæ, that is as compounds of mercuric oxide with the chloride, iodide, acetate, &c., of dimercurammonium, or they may be formulated as compounds of mercuric salts with trimercuramine (p. 917). The tetrammonium salts are also produced by the water of ammonium-salts on mercuric oxide. (**Hirzel**, lxxxiv. 258), and in other reactions, as will be presently mentioned.

Acetate of Tetramercurammonium. $\mathrm{C}^4\mathrm{H}^6(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2)''\mathrm{O}^4.2\mathrm{H}^2\mathrm{O}$ (λ).—Crystallised compound obtained by treating mercuric oxide with acetate of ammonium. When dried at 100° it leaves a yellowish-white powder.

The *arsenate* is a white salt, obtained by boiling mercuric oxide with arsenate of ammonium.

Bromate. $(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2)\mathrm{Br}^2\mathrm{O}^6.2\mathrm{H}^2\mathrm{O}$, (ι).—This salt separates slowly from an aqueous solution of mercuric bromate slightly supersaturated with ammonia, bromate of ammonium remaining in solution. When heated in a glass tube, even in very small quantity, it detonates with great violence, metallic mercury being scattered about. (**Rammelsberg.**)

Carbonate. $(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2)\mathrm{CO}^3.4\mathrm{H}^2\mathrm{O}$(χ).—Obtained by passing carbonic acid gas through water, in which hydrate of tetramercurammonium is suspended, as a pale yellow powder, which may be washed with cold water without decomposition (**Millon**). Hirzel, by boiling finely-divided mercuric oxide with excess of carbonate of ammonium, obtained a salt having the same composition, but with ½ at. water more. It was yellowish-white when dry, turned grey when exposed to light, was not decomposed by potash, but gave off all its nitrogen as ammonia when boiled with aqueous iodide or sulphide of potassium. By treating mercuric oxide with an excess of cold aqueous carbonate of ammonium, Hirzel obtained a white pulverulent salt containing $(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2)\mathrm{CO}^3.\mathrm{H}^2\mathrm{O}$ (π); when exposed to light it quickly decomposed, assuming a grey colour.

Millon's carbonate of tetramercurammonium may be washed with water without decomposition. When perfectly dry, it may be heated without alteration to 130°, but at higher temperatures it gives off a considerable quantity of water. At 145° it assumes a slight brown tint, not however giving off any more water at that temperature; but if the heat be raised to 180–200°, more water is given off together with a large quantity of ammonia; the residue has a deep yellow colour and contains a considerable quantity of carbonic acid, but does not effervesce with acids. This residue is decomposed by strong hydrochloric acid, which eliminates a gas from it, with decrepitation.

Chloride. $\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2\mathrm{Cl}^2.2\mathrm{H}^2\mathrm{O}$ (ω).—Obtained by subjecting chloride of dimercurammonium (infusible white precipitate) to prolonged washing with cold water, or better by boiling it with water:

$$2\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^2\mathrm{H}^4\mathrm{N}^2\mathrm{Cl}^2 = \overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2\mathrm{Cl}^2 + 2\mathrm{H}^4\mathrm{NCl};$$

also by treating the chloride of dimercurammonium with potash or soda. It is a heavy granular, yellow powder which turns white again when treated with sal-ammoniac. (**Kane.**)

Chromate. $(\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2)\mathrm{CcrO}^4.2\mathrm{H}^2\mathrm{O}$, (υ).—A solution of chromate of ammonium does not act on mercuric oxide in the cold; but converts it at the boiling heat into a compound of chromate of tetramercurammonium with 3 at. mercuric chromate $(\mathrm{Hhg}''\mathrm{CcrO}^4)$, which when boiled with aqueous iodide or sulphide of potassium, gives off all its nitrogen in the form of ammonia, and when drenched with ammonia, is converted into a lemon-yellow chromate of tetramercurammonium having the composition above indicated.

Hydrate. $\left.\begin{matrix}\overset{\prime\prime}{\mathrm{H}}\mathrm{hg}^4\mathrm{N}^2\\ \mathrm{H}^2\end{matrix}\right\}\mathrm{O}^2$, (θ).—This compound is obtained either by treating mercuric oxide with aqueous ammonia, or by heating a salt of tetramercurammonium with a caustic alkali. Yellow mercuric oxide obtained by precipitation is rapidly acted on by ammonia; the red modification but slowly; the product of the action of ammonia on the latter retains the crystalline character of the oxide itself. By washing the hydrate obtained by either process with water, then pressing it between bibulous paper, and drying it over oil of vitriol in a vacuum, or exposing it to a temperature of 130°; it is obtained as a brown powder containing $\left.\begin{matrix}H\overset{\prime\prime}{h}g^4N^2\\H^2\end{matrix}\right\}O^2.H^2O$, (*o*). By drying it over quicklime under a bell-jar, it is obtained as a yellow substance containing $\left.\begin{matrix}H\overset{\prime\prime}{h}g^4N^2\\H^2\end{matrix}\right\}O^2.4H^2O$, (*κ*). The product prepared from the yellow oxide parts with its water much more readily than that obtained from the red oxide.

The dark brown compound $\left.\begin{matrix}H\overset{\prime\prime}{h}g^4N^2\\H^2\end{matrix}\right\}O^2.H^2O$ (the so-called *anhydrous mercuramine*), which may also be represented as a compound of oxide of dimercurammonium with mercuric oxide $H\overset{\prime\prime}{h}g^2H^4N^2O.2Hhg''O$, or as a hydoramine (i. 197) containing $\left.\begin{matrix}H\overset{\prime\prime}{h}g^4\\H^4\end{matrix}\right\}\begin{matrix}N^2\\O^2\end{matrix}$, is not altered by contact with the air. The yellow more highly hydrated compound, on the other hand, absorbs carbonic acid rapidly from the air and turns white, being converted into carbonate of tetramercurammonium. It is insoluble in *water* and in *alcohol*, gives off ammonia when boiled with *potash*, but requires long boiling to complete the decomposition. The brown compound is decomposed by fusion with *hydrate of potassium* into nitrogen, metallic mercury, and mercuric oxide.

Hydrate of tetramercurammonium dissolves very easily in *acids*, forming the salts of tetrammonium. It expels ammonia very readily from its salts like lime. It dissolves very easily with brisk evolution of ammonia gas, in a hot solution of *nitrate of ammonium*, and the solution deposits, on cooling, a considerable quantity of white crystals, which are decomposed by water, yielding a greenish-yellow powder. It dissolves also with equal facility in a hot solution of *sal-ammoniac*, with evolution of ammonia, and separation of a white powder insoluble in water.

Iodate.—By digesting mercuric iodate with ammonia, Millon obtained a salt of variable composition which decomposed at about 180°, with detonation and formation of mercuric iodide.

Iodide. $H\overset{\prime\prime}{h}g^4N^2I^2.2H^2O$, (*ω*).—This compound may be formed in several ways.—1. By heating mercuric iodide with excess of ammonia:

$$4H\overset{\prime\prime}{h}gI^2 + 8H^3N + 2H^2O = H\overset{\prime\prime}{h}g^4N^2I^2 2H^2O + 6H^4NI.$$

Iodide of hydrogen and dimercurammonium is formed at the same time and dissolves in the hot liquid, while the iodide of tetramercurammonium remains in the form of a brown powder. To obtain it pure, the liquid must be decanted before it begins to deposit crystals, and the brown residue again boiled several times with fresh ammonia, till the filtered liquid no longer deposits crystals on cooling.—2. By passing ammonia-gas over mercuric oxy-iodide:

$$H\overset{\prime\prime}{h}g^4I^2O^3 + 2H^3N = H\overset{\prime\prime}{h}g^4N^2I^2.2H^2O + H^2O.$$

3. By digesting the chloride of tetramercurammonium in aqueous iodide of potassium (Rammelsberg); adding ammonia to a solution of iodide of mercury and potassium mixed with caustic potash (Nessler, Chem. Gaz. 1856, pp. 445, 463):

$$4Hhg''K^2I^4 + 2H^3N + 6KHO = H\overset{\prime\prime}{h}g^4N^2I^2.2H^2O + 14KI + 4H^2O.$$

This last reaction affords an extremely delicate test for ammonia. A solution of iodide of mercury and potassium is prepared by adding iodide of potassium to a solution of corrosive sublimate till a portion only of the resulting red precipitate is redissolved, then filtering, and mixing the filtrate with caustic potash. The liquid thus obtained produces a brown precipitate with a very small quantity of ammonia, either free or in the form of an ammoniacal salt. The precipitate is soluble in excess of iodide of potassium. (Nessler.)

Iodide of tetramercurammonium is a powder of a brown colour inclining to purple-red. It gives off a small quantity of water at 128°, and if more strongly heated out of contact with the air, it melts to a dark brown liquid, and is then decomposed with a blue light and violent explosion, yielding water, metallic mercury, mercuric iodide, ammonia, and nitrogen, without leaving any residue. Heated with aqueous *sulphide of barium*, it gives off all its nitrogen in the form of ammonia. In a stream of *hydrochloric acid gas*, it turns yellow in parts, gives off white fumes, and at a higher temperature yields a sublimate of ammonio-mercuric iodide, mercuric chloride, chloride of ammonium, and iodide of ammonium. It dissolves easily in warm *hydrochloric acid*, forming a colourless liquid, which, when concentrated, deposits on cooling red crystals of mercuric iodide, and yellow crystals of mercuric iodochloride.

Nitrate. $\mathrm{H\overset{\prime\prime}{h}g^4N^2(NO^3)^2.2H^2O}$, (like ι).—Obtained by mixing a hot dilute solution of mercuric nitrate with a slight excess of ammonia, as a white granular powder, which, when heated, turns yellow, gives off nitrogen and ammonia, then nitrous acid, and finally oxygen and mercury. It is altered by boiling *potash;* dissolves in cold *hydrochloric acid*, and is separated from the solution by water; dissolves sparingly and without decomposition in *nitric* and *sulphuric acids;* dissolves also in *ammonia*, and is partially precipitated from the solution by water. (Soubeiran.)

A yellow crystalline double salt consisting of *nitrate of ammonium and tetramercurammonium*, $\mathrm{\left.\begin{matrix}H\overset{\prime\prime}{h}g^4N^2\\2H^4N\end{matrix}\right\}(NO^3)^4.2H^2O}$ (ξ), is obtained, according to Mitscherlich, by mixing nitrate of trimercurammonium (p. 917) with excess of ammonia, and adding nitrate of ammonium, which dissolves a portion of the salt. As the solution cools and the ammonia evaporates, the double salt separates in crystalline plates.

Oxalate. $\mathrm{C^2(H\overset{\prime\prime}{h}g^4N^2)O^4.2H^2O}$, ($\tau$).—Obtained by digesting mercuric oxalate with excess of ammonia and washing the product till the liquid no longer exhibits any alkaline reaction (Millon); or by digesting mercuric oxide in the cold with oxalate of ammonium (Hirzel). It is a white, loose, amorphous powder which explodes when heated.

Phosphate. $\mathrm{\left.\begin{matrix}(H\overset{\prime\prime}{h}g^4N^2)\\H\overset{\prime\prime}{h}g^2\end{matrix}\right\}P^2O^8.2H^2O}$, ($\mu$).—Obtained by treating mercuric oxide with a boiling solution of tri-ammonic phosphate. It is a white salt which is not decomposed by potash, but gives off ammonia when treated with iodide or sulphide of potassium. (Hirzel.)

Sulphate. $\mathrm{(H\overset{\prime\prime}{h}g^4N^2)SO^4.2H^2O}$, ($\sigma$).—*Ammoniacal turpethum.* This salt, first obtained by Fourcroy, and subsequently analysed by Kane, is prepared by dissolving mercuric sulphate in ammonia and precipitating the solution with water. Ammonia takes up a very large quantity of mercuric sulphate, and when a perfectly saturated solution is left to evaporate in the air or over oil of vitriol, its surface becomes covered with crystalline crusts, consisting of small, hard, highly lustrous crystals of ammoniacal turpethum (Millon). The salt may also be obtained, according to Ullgren, by digesting basic mercuric sulphate (*mineral turpethum*) with sulphate of ammonium till the insoluble portion becomes white.

Sulphate of tetramercurammonium is a white heavy powder, yellowish when dry, when heated it turns brown and is resolved into water, nitrogen, a small quantity of ammonia, and mercurous sulphate. By sulphydric acid it is converted into mercuric sulphide and neutral sulphate of ammonium. It dissolves in hydrochloric and in nitric acid, very slightly in water.

Some of the basic salts already described as produced by the decomposition of sulphate of ammonium and dimercurammonium, may also be regarded as tetramercurammonium-salts (see p. 917).

Mercurous Bases.

Mercurosammonium. $\mathrm{\left.\begin{matrix}Hhg'\\H^3\end{matrix}\right\}N}$.—The chloride of this base, $\mathrm{Hhg'H^3NCl}$, is the black substance formed when dry calomel is exposed to the action of ammonia-gas. When exposed to the air, it gives off ammonia and leaves white mercurous chloride.

Dimercurosammonium. $\mathrm{\left.\begin{matrix}H\overset{\prime}{h}g^2\\H^2\end{matrix}\right\}N}$;—The *chloride*, $\mathrm{(H\overset{\prime}{h}g^2H^2N)Cl}$, is formed by digesting calomel in aqueous ammonia, sal-ammoniac being formed at the same time:

$$\mathrm{2HhgCl + 2H^3N = (Hhg^2H^2N)Cl + H^3NCl.}$$

It is grey when quite dry, and is not altered by boiling water. Kane, who analysed this compound, regarded it as *mercurous amido-chloride*, $\mathrm{HhgCl.HhgNH^2}$.

Nitrate of Dimercurosammonium. $\mathrm{2(Hhg^2H^2N)NO^3.H^2O}$. This, according to Kane, is the composition of the velvet-black precipitate, known as *Hahnemann's soluble mercury*, which is produced on adding ammonia to a solution of mercurous nitrate. According to C. G. Mitscherlich, on the other hand, the precipitate thus formed has the composition $\mathrm{3Hhg^2O.N^2O^5.2NH^3}$, which is that of a nitrate of trimercurosammonium $\mathrm{2(H\overset{\prime}{h}g^3HN)NO^3.2H^2O}$.

A clearer view of the composition and relations of the ammoniacal mercury-compounds is afforded by the following method of classification, suggested by Mr. G. C. Foster, in which the greater number of these compounds are represented as hydoramines (i. 197), that is, as bodies formed on the mixed type, $\left.\begin{matrix}m\mathrm{H^3N}\\n\mathrm{H^2O}\end{matrix}\right\}$, and the rest as hydrochloramines, $\left.\begin{matrix}m\mathrm{H^3N}\\n\mathrm{HCl}\end{matrix}\right\}$, hydriodamines, &c. This view of the composition of the ammoniacal mercuric compounds is exhibited in the following table, in which the Greek letters placed under the formulæ correspond to those attached to the names of the compounds in the preceding pages (916–920):

$$\text{Type }\left.\begin{matrix}m\mathrm{H^3N}\\n\mathrm{HCl}\end{matrix}\right\}$$

$$\left.\begin{matrix}m=1\\n=1\end{matrix}\right\}\quad\underset{\alpha}{\left.\begin{matrix}\mathrm{Hhg''}\\\mathrm{H^2}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{Cl}\end{matrix}}\;\Big\|\;\left.\begin{matrix}m=1\\n=2\end{matrix}\right\}\quad\underset{\beta}{\left.\begin{matrix}\mathrm{Hhg''}\\\mathrm{H^3}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{Br^2}\end{matrix}}\quad\underset{\gamma}{\left.\begin{matrix}\mathrm{Hhg''}\\\mathrm{H^3}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{Cl^2}\end{matrix}}\quad\underset{\delta}{\left.\begin{matrix}\mathrm{Hhg''}\\\mathrm{H^3}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{I^2}\end{matrix}}$$

$$\left.\begin{matrix}m=2\\n=2\end{matrix}\right\}\quad\underset{\epsilon}{\left.\begin{matrix}\mathrm{Hhg''}\\\mathrm{H^6}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{Cl^2}\end{matrix}}\quad\underset{\zeta}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^2}\\\mathrm{H^4}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{Cl^2}\end{matrix}}\quad\underset{\eta}{\left.\begin{matrix}\mathrm{Hhg''}\\\mathrm{H^6}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{I^2}\end{matrix}}$$

$$\text{Type }\left.\begin{matrix}m\mathrm{H^3N}\\n\mathrm{H^2O}\end{matrix}\right\}$$

$$\left.\begin{matrix}m=1\\n=1\end{matrix}\right\}\quad\underset{\theta}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^2}\\\mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{O}\end{matrix}}$$

$$\left.\begin{matrix}m=1\\n=2\end{matrix}\right\}\quad\underset{\iota}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^2}\\\mathrm{H^2}\\\mathrm{(BrO^2)'}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{O^2}\end{matrix}}\;\Big\|\;\left.\begin{matrix}m=1\\n=3\end{matrix}\right\}\quad\underset{\kappa}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^2}\\\mathrm{H^5}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{O^3}\end{matrix}}\quad\underset{\lambda}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^2}\\\mathrm{H^4}\\\mathrm{C^2H^3O}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{O^3}\end{matrix}}$$

$$\left.\begin{matrix}m=1\\n=4\end{matrix}\right\}\quad\underset{\mu}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^3}\\\mathrm{H^2}\\\mathrm{(PO)'''}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{O^4}\end{matrix}}\;\Big\|\;\left.\begin{matrix}m=2\\n=3\end{matrix}\right\}\quad\underset{\nu}{\left.\begin{matrix}\mathrm{Hhg''}\\\mathrm{H^8}\\\mathrm{(SO^2)''}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^3}\end{matrix}}$$

$$\left.\begin{matrix}m=2\\n=3\end{matrix}\right\}\quad\underset{\xi}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^2}\\\mathrm{H^6}\\\mathrm{(NO^2)^2}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^3}\end{matrix}}\quad\underset{o}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^4}\\\mathrm{H^4}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^3}\end{matrix}}\quad\underset{\pi}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^4}\\\mathrm{H^2}\\\mathrm{(CO)''}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^3}\end{matrix}}$$

$$\left.\begin{matrix}m=2\\n=4\end{matrix}\right\}\quad\underset{\rho}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^3}\\\mathrm{H^6}\\\mathrm{(NO^2)^2}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^4}\end{matrix}}\quad\underset{\sigma}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^4}\\\mathrm{H^4}\\\mathrm{(SO^2)''}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^4}\end{matrix}}\quad\underset{\tau}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^4}\\\mathrm{H^4}\\\mathrm{(C^2O^2)''}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^4}\end{matrix}}\quad\underset{\upsilon}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^4}\\\mathrm{H^4}\\\mathrm{(CrO^2)''}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^4}\end{matrix}}$$

$$\left.\begin{matrix}m=2\\n=5\end{matrix}\right\}\quad\underset{\phi}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^5}\\\mathrm{H^4}\\\mathrm{(SO^2)''}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^5}\end{matrix}}\;\Big\|\;\left.\begin{matrix}m=2\\n=6\end{matrix}\right\}\quad\underset{\chi}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^4}\\\mathrm{H^8}\\\mathrm{(CO)''}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^6}\end{matrix}}\;\Big\|\;\left.\begin{matrix}m=4\\n=7\end{matrix}\right\}\quad\underset{\psi}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^7}\\\mathrm{H^8}\\\mathrm{(SO^2)^2}\end{matrix}\right\}\begin{matrix}\mathrm{N^4}\\\mathrm{O^7}\end{matrix}}$$

$$\text{Type }\begin{matrix}m\mathrm{H^3N}\\n\mathrm{HCl}\\o\mathrm{H^2O}\end{matrix}$$

$$\left.\begin{matrix}m=1\\n=1\\o=1\end{matrix}\right\}\quad\underset{\omega}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^2}\\\mathrm{H^3}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{I}\\\mathrm{O}\end{matrix}}\;\Big\|\;\left.\begin{matrix}m=1\\n=1\\o=2\end{matrix}\right\}\quad\underset{\alpha'}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^3}\\\mathrm{H^2}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{Cl}\\\mathrm{O^2}\end{matrix}}\;\Big\|\;\left.\begin{matrix}m=2\\n=2\\o=3\end{matrix}\right\}\quad\underset{\beta'}{\left.\begin{matrix}\mathrm{H\overset{\prime\prime}{h}g^5}\\\mathrm{H^4}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{Cl^2}\\\mathrm{O^3}\end{matrix}}$$

The mercurous compounds may be formulated in a similar manner, *e.g.*:

Chloride of Mercurosammonium . . . . $\left.\begin{matrix}\mathrm{Hhg'}\\\mathrm{H^3}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{Cl}\end{matrix}$

Chloride of Dimercurosammonium . . . . . . $\left.\begin{matrix}\mathrm{H\overset{\prime}{h}g^2}\\\mathrm{H^2}\end{matrix}\right\}\begin{matrix}\mathrm{N}\\\mathrm{Cl}\end{matrix}$

Nitrate " . . . . . . $\left.\begin{matrix}\mathrm{H\overset{\prime}{h}g^4}\\\mathrm{H^6}\\\mathrm{(NO^2)^2}\end{matrix}\right\}\begin{matrix}\mathrm{N^2}\\\mathrm{O^3}\end{matrix}$

MERCURY-RADICLES, ORGANIC. (Frankland [1852], Ann. Ch. Pharm. lxxxv. 381.—Dünhaupt, Chem. Gaz. 1854, pp. 263-292.—Strecker, Compt. rend. xxxix. 57.—Buckton, Ann. Ch. Pharm. cviii. 103; cix. 218; Chem. Soc. J. xvi. 17.—Frankland and Duppa, *ibid.* xvii. 415.)

Mercury unites with alcohol-radicles of the series, C^nH^{2n+1}, viz. methyl, ethyl, and amyl,—also with allyl C^3H^5,—forming compounds into which it enters as a diatomic element. These compounds may, in fact, be regarded as formed from inorganic mercuric compounds, such as the chloride, bromide, &c., by substitution of an alcohol-radicle for either the half or the whole of the chlorine, &c.,: thus

Mercuric chloride.	Mercuric chlorethide.	Mercuric ethide.
$Hhg''\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	$Hhg''\left\{\begin{matrix}C^2H^5\\Cl\end{matrix}\right.$	$Hhg''\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.$

When both atoms of chlorine, &c., are completely replaced by an alcohol-radicle, the product is an indifferent compound (a neutral mercuric ether) incapable of uniting with acids or acid elements. But when only half of the chlorine, or other chlorous radicle is thus replaced, there results a saline compound, that is to say, a substance which easily undergoes double decomposition, and in which the residue united with the chlorine ($Hhg''C^2H^5$ for example), plays the part of a monatomic radicle.

The two kinds of compounds here considered, are in fact related to mercury, in the same manner as mercaptan and ethylic sulphide are related to sulphur,—mercuric ethide, for example, being the ethylic ether of mercuric chlorethide, just as sulphide of ethyl is the ethylic ether of mercaptan.

Mercaptan.	Ethylic sulphide.	Mercuric chlorethide.	Mercuric ethide.
$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}S$	$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}S$	$\left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\}Hhg$	$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}Hhg$

There is, however, this difference between the two classes of compounds, that in mercuric chlorethide and its analogues, in which only 1 at. chlorine &c. is replaced by an alcohol radicle, the remaining chlorous atom is most easily replaced by another chlorous radicle, whereas, in the corresponding sulphur-compounds, the remaining hydrogen-atom, being basylous, is most easily replaced by metals or other basylous elements.

If the mercury in these compounds be regarded as monatomic, those which contain only mercury and an alcohol-radicle must be represented by formulæ of the type HgC^nH^{2n+1}; and those which contain iodine, chlorine, &c. as compounds of these radicles with mercuric iodide, chloride, &c.; *e.g.* HgC^2H^5, *mercurethyl* or *hydrargethyl;* $Hg^2C^2H^5I$ or $HgC^2H^5.HgI$, *iodide*, or rather *mercuriodide, of mercurethyl*, &c.; but the former mode of representation affords a much simpler and more satisfactory view of their relations.

Formation of the Alcoholic Mercury-compounds.—These compounds may be obtained by four different processes:—1. By the action of mercury on the iodide of an alcohol-radicle, under the influence either of diffused daylight or of direct sunshine; combination then takes place, and an iodo-mercuric compound is produced (Frankland, Strecker):

$$Hhg'' + C^nH^{2n+1}I = Hhg''\left\{\begin{matrix}C^nH^{2n+1}\\I\end{matrix}\right. .$$

2. By the action of mercuric chloride on a zinc-compound of an alcohol-radicle, the product being an organo-mercuric compound, containing either 2 at. of the alcohol-radicle, or 1 at. alcohol-radicle and 1 at. chlorine, according as one or other of the reagents is in excess (Buckton):

$$Hhg''Cl^2 + Zzn''(C^nH^{2n+1})^2 = Hhg''(C^nH^{2n+1})^2 + Zzn''Cl^2,$$

$$2Hhg''Cl^2 + Zzn''(C^nH^{2n+1})^2 = 2\left[Hhg''\left\{\begin{matrix}C^nH^{2n+1}\\Cl\end{matrix}\right.\right] + Zzn''Cl^2.$$

3. By the action of mercuric chloride on the organo-bismuth compounds containing 3 at. of an alcohol-radicle; thus bismutho-triethide (i. 596) treated with mercuric chloride yields bismutho-dichlorethide and mercuric chlorethide (Dünhaupt):

$$\overset{'''}{Bi}(C^2H^5)^3 + 2Hhg''Cl^2 = \overset{'''}{Bi}(C^2H^5)Cl^2 + 2Hhg''(C^2H^5)Cl.$$

4. By the action of sodium-amalgam on the iodides of the alcohol-radicles in presence of acetic ether (Frankland and Duppa). The reaction is represented by the equation:

$$2C^nH^{2n+1}I + Na^2 + Hhg'' = Hhg''(C^nH^{2n+1})^2 + 2NaI.$$

The acetic ether appears to take no part in the reaction, but remains in undiminished quantity at the end of the process. Nevertheless, the presence of this or a similar ether (viz. methylic acetate or ethylic formate) is essential to the success of the process, inasmuch as sodium-amalgam does not act on the alcoholic iodides when simply placed in contact or heated with them; neither is the reaction induced by the presence of ethylic ether, but on adding a few drops of acetic ether, it takes place immediately. The proportion of sodium in the amalgam must be very small, not exceeding 1 pt. to 500 of mercury. If a solid or semi-solid amalgam is used, the reaction proceeds in quite a different manner.

This is by far the best mode of preparing the alcoholic mercury-compounds, yielding in a short time large quantities of the methyl-, ethyl-, and amyl-compounds. Mercuric iodethide and iodomethide are obtained with tolerable facility by the first method above-mentioned; but the corresponding amyl-compound was obtained in this way only in quantities barely sufficient for its identification. On the other hand, to obtain mercuric ethide and methide by the second method, requires the previous preparation of very large quantities of the corresponding zinc-compounds, and the preparation of mercuric amylide has never been attempted by a similar process, on account of the great difficulty of preparing zinc-amyl. (Frankland and Duppa.)

The mercury-compounds containing 2 at. of an alcohol-radicle, are easily converted, by the action of bromine, chlorine, or iodine, into compounds containing only 1 at. of an alcohol-radicle, *e.g.*:

$$\underset{\text{Mercuric ethide.}}{Hhg''(C^2H^5)^2} \quad + \quad Br^2 \quad = \quad \underset{\text{Mercuric bromethide.}}{Hhg''(C^2H^5)Br} \quad + \quad \underset{\text{Ethylic bromide.}}{C^2H^5Br}$$

A similar action is exerted by acids. *e.g.* by hydrobromic acid:

$$\underset{\text{Mercuric ethide.}}{Hhg''(C^2H^5)^2} \quad + \quad HBr \quad = \quad \underset{\text{Mercuric bromethide.}}{Hhg''(C^2H^5)Br} \quad + \quad \underset{\text{Ethylic hydride.}}{C^2H^5.H.}$$

With sulphuric acid, in like manner, the products are mercuric sulphatethide, $Hhg''^2\left\{\begin{matrix}(C^2H^5)^2\\(SO^4)''\end{matrix}\right.$ and ethylic hydride.

A precisely similar action is exerted by certain salts. When, for example, mercuric chloride acts upon mercuric ethide, the latter gives up half its ethyl for half the chlorine of the former, producing 2 at. mercuric chlorethide:

$$Hhg''(C^2H^5)^2 \quad + \quad Hhg''Cl^2 \quad = \quad 2Hhg''(C^2H^5)Cl.$$

On the other hand, the mercuric compounds containing only 1 at. of an alcohol-radicle are easily converted into others containing 2 at. of an alcohol-radicle: thus, mercuric iodethide and zinc-ethyl act upon one another in such a manner as to yield mercuric ethide and iodide of zinc:

$$2Hhg''(C^2H^5)I \quad + \quad Zzn''(C^2H^5)^2 \quad = \quad 2Hhg''(C^2H^5)^2 \quad + \quad Zzn''I^2.$$

The mercury compounds containing 2 at. of an alcohol-radicle are converted into the corresponding zinc-compounds when heated with excess of finely-granulated zinc (Frankland and Duppa, Chem. Soc. J. xvii. 29):

$$Hhg''(C^nH^{2n+1})^2 \quad + \quad Zzn^2 \quad = \quad Zzn''(C^nH^{2n+1})^2 \quad + \quad ZznHhg.$$

Allyl-compound.

Mercuric Iodallylide. $Hhg''\left\{\begin{matrix}C^3H^5\\I\end{matrix}\right.$.—When iodide of allyl is agitated with mercury, a yellow crystalline mass is formed, from which the mercuric iodallylide may be extracted by hot alcohol or ether. The alcoholic solution deposits it on cooling in silvery scales, which turn yellow when exposed to light, especially on drying. It is sparingly soluble in cold alcohol, nearly insoluble in water. It sublimes at 100°, in white shining rhombic plates, melts at 135°, and solidifies on cooling to a yellow crystalline mass. If more quickly and strongly heated, it decomposes for the most part, leaving a carbonaceous residue, and giving off a yellow sublimate.

The alcoholic solution is decomposed by nitrate of silver, the whole of the iodine being separated as iodide of silver; oxide of silver likewise decomposes it, forming iodide of silver and a strongly alkaline solution which, on evaporation, yields a syrupy strongly alkaline mass, soluble in water, and forming salts with acids. This product is probably mercuric allyl-hydrate, or hydrate of mercurallyl, $Hhg''\left\{\begin{matrix}C^3H^5\\HO\end{matrix}\right.$. (Zinin, Ann. Ch. Pharm. xcvi. 393.)

Mercuric iodallylide is easily decomposed by hydriodic acid and by iodine. The following equations represent respectively the action which takes place in each case:

$$(1).\quad HhgC^3H^5I + HI \quad = \quad HhgI^2 + C^3H^6$$

$$(2).\quad HhgC^3H^5I + II \quad = \quad HhgI^2 + C^3H^5I.$$

Berthelot's process for preparing tritylene, by means of iodide of allyl, mercury, and hydrochloric acid, depends on the first of these reactions. (Linnemann, Ann. Ch. Pharm. cxxxiii. 133.)

Amyl-compounds.

Mercuric Amylide. $Hhg''\left\{\begin{matrix}C^5H^{11}\\C^5H^{11}\end{matrix}\right.$.—This compound is obtained by the action of sodium-amalgam on iodide of amyl, in presence of acetic ether. 5 pts. by weight of amylic iodide, and 1 pt. acetic ether are agitated with sodium-amalgam in a vessel externally cooled; the product is distilled over a water-bath to separate the acetic ether, and a current of steam then passed into the retort until about half the heavy liquid has distilled over. The residual liquid, after washing with water and drying over chloride of calcium, consists of pure mercuric amylide.

This compound is a colourless, transparent, mobile liquid, of specific gravity 1·6663 at 0°. It has a very faint amylic odour, and leaves a persistent taste upon the palate, resembling that produced by other organo-mercurial compounds. It cannot be distilled, even in vacuo, without partial decomposition. It can bear a temperature of 140°, but long before its boiling point is reached, mercury separates from it in considerable quantity. It may, however, be distilled with water without decomposition. It is insoluble in *water*, and very slightly soluble in *alcohol*, but dissolves readily in *ether*. Exposed to the *air* it suffers no oxidation, but when allowed to fall into *chlorine*, it immediately produces dense white fumes of mercuric chloro-amylide. Brought into contact with solid *iodine*, it hisses like red-hot iron immersed in water The reaction with *bromine* is still more violent. (Frankland and Duppa.)

Mercuric Chloramylide, $Hhg''\left\{\begin{matrix}C^5H^{11}\\Cl\end{matrix}\right.$, is readily obtained by treating mercuric amylide with alcoholic solution of mercuric chloride in excess. It closely resembles the iod-amylide (*vid. inf.*) in its properties, is insoluble in water, but very freely soluble in hot alcohol and ether. From its alcoholic solution it crystallises in beautiful hair-like needles, which can be sublimed at a gentle heat without decomposition. It melts at 86°, and has the appearance of a heavy oil, perfectly limpid and colourless. It retains any excess of corrosive sublimate with the greatest obstinacy, repeated washings with alcohol and water not being sufficient to remove it. It may, however, be purified by dissolving it repeatedly in alcohol and reprecipitating with water. (Frankland and Duppa.)

Mercuric Iodamylide. $Hhg''\left\{\begin{matrix}C^5H^{11}\\I\end{matrix}\right.$.—An ethereal solution of mercuric amylide, treated first with alcoholic solution of iodine, and then with solid iodine, nearly solidifies to a crystalline mass of mercuric iod-amylide, iodide of amyl being at the same time produced:

$$Hhg''\left\{\begin{matrix}C^5H^{11}\\C^5H^{11}\end{matrix}\right. + I^2 = Hhg''\left\{\begin{matrix}C^5H^{11}\\I\end{matrix}\right. + C^5H^{11}I.$$

On washing the crude product with weak alcohol, pressing between folds of blotting paper, and recrystallising from hot alcohol, mercuric iod-amylide is deposited in small pearly scales, which are not very soluble in *alcohol*, but freely soluble in *ether*. If a few drops of alcoholic potash are added to a boiling saturated alcoholic solution of these crystals, and the liquid left to cool, no crystals appear for some time; but ultimately large pearly plates are deposited, which have the same composition as the small scaly crystals above mentioned, and reproduce them when washed with water and redissolved in alcohol. Mercuric iod-amylide is slightly soluble in boiling *water*, and separates therefrom on cooling in minute crystals which appear as an opalescent cloud in the liquid. It melts at 122°, and on cooling solidifies to a white crystalline mass, having the appearance of stearin; at 140° it begins to turn yellow from formation of mercurous iodide. In a moderately heated current of air, it may be sublimed without change. It is but partially decomposed by *alcoholic potash:* Heated with *zinc* to 130° in a sealed tube it yields zinc-amyl and zinc-amalgam. (Frankland and Duppa.)

Ethyl-compounds.

Strecker, by acting on iodide of ethyl with mercury, obtained the compound $Hg^2C^2H^5I$ or $Hhg''C^2H^5I$, originally designated as *iodide of mercurethyl*, or *iodide of hydrargethyl*, but now called *mercuric iodethide*. Dünhaupt obtained the corresponding chlorine- and bromine-compounds, by decomposing bismutho-triethide with mercuric chloride or bromide, and prepared therefrom several of the other salts. Buckton obtained mercuric ethide $Hg^2(C^2H^5)^2$ or $Hhg''(C^2H^5)^2$, by the action of zinc-ethyl on mercuric iodethide or on mercuric chloride (pp. 921, 922); and lastly Frankland and Duppa have shown that this compound may be more easily obtained by the action of sodium-amalgam on iodide of ethyl, in presence of acetic ether.

Mercuric Bromethide. $Hhg''(C^2H^5)Br$.—Obtained by the action of mercuric bromide on bismutho-triethide, or by treating mercuric hydro-ethide with hydrobromic acid, or an alcoholic solution of the hydro-ethide with alcoholic bromine. It resembles the chlorethide. (Dünhaupt.)

Mercuric Carbonethide. Carbonate of mercurethyl.—Prepared by decomposing the chlorethide with carbonate of silver at a gentle heat. It crystallises with difficulty and is easily decomposed by heat. Acids decompose it, with evolution of carbonic anhydride. (Dünhaupt.)

Mercuric Chlorethide. $Hhg''(C^2H^5)Cl$.—Obtained by the action of mercuric chloride on bismutho-triethide (Dünhaupt); by precipitating the aqueous solution of the nitrethide with chloride of sodium (Strecker); and by treating mercuric ethide with alcoholic solution of mercuric chloride in excess (Frankland and Duppa). It is nearly insoluble in *water*, dissolves sparingly in *ether*, and in cold alcohol, but freely in boiling *alcohol*, and crystallises therefrom in light iridescent laminæ, having a silvery lustre. When heated to 40° it sublimes in thin laminæ, without previous fusion, but at 100° it melts to a clear oily liquid, and then evaporates completely. Heated on platinum-foil it burns with a faint flame, diffusing a very unpleasant odour. (Dünhaupt.)

Mercuric Cyanethide. $Hhg''(C^2H^5)Cy$.—Formed by saturating an alcoholic solution of mercuric hydrethide with strong hydrocyanic acid. Crystallises readily. Very volatile; when heated in a tube, it emits a vapour which has an extremely repulsive odour, attacks the respiratory organs strongly, and appears to be highly poisonous; a carbonaceous residue is left in the tube. The cyanide dissolves readily in alcohol and ether. (Dünhaupt.)

Mercuric Ethide. $Hhg''(C^2H^5)^2$.—This compound is prepared:—1. By the action of zinc-ethyl on mercuric iodethide. Dry pulverised mercuric iodethide is added by small quantities to zinc-ethyl contained in a retort through which a stream of coal-gas is passing, the mixture being incorporated by stirring, and, as soon as the zinc-ethyl is saturated—which may be known by the stirring rod ceasing to fume on exposure to the air—the product is distilled till nothing but gases pass over. The distillate, which is a heavy liquid, mixed with a little ether, is then redistilled with a slight excess of zinc-ethyl, to ensure complete decomposition of the iodethide, then washed with hydrochloric acid, and afterwards with water, and rectified (Buckton).—2. By heating zinc-ethyl with mercuric chloride, avoiding an excess of the latter, as otherwise mercuric chlorethide will be formed: the slight excess of zinc-ethyl is decomposed by water, and the separated oxide of zinc dissolved out by dilute hydrochloric acid. (Buckton.)

3. A mixture of 16 pts. by weight of iodide of ethyl and 1 pt. of acetic ether is poured upon sodium-amalgam, the flask being alternately agitated to promote the reaction, and plunged into cold water to moderate the rise of temperature. The completion of the reaction is known by the subsidence of the temperature, and the absence of more than traces of precipitated iodine, when a few drops of the clear liquid remaining in the flask are boiled with nitric acid. When the quantity of iodide of sodium formed has been increased so far as to render the ethereal liquid pasty, thereby preventing a sufficiently intimate contact with the amalgam, it is advisable to place the flask in a water-bath, and distil off the more volatile portion of the contents, to be again acted on by fresh amalgam.* If this distillation be deferred till the residue has become decidedly thick and pasty, it will not be necessary to repeat it, as the distillate will remain sufficiently fluid up to the termination of the reaction. The product mixed with water separates into two layers, the ethereal liquid either floating or sinking in the aqueous solution of iodide of sodium, according to the degree of concentration or the latter. It is then successively treated with alcoholic potash, washed with water, dried over chloride of calcium, and rectified. (Frankland and Duppa.)

4. Buckton likewise obtained mercuric ethide by the action of cyanide of potassium on the iodethide:

$$2Hhg(C^2H^5)I + 2KCy = Hhg(C^2H^5)^2 + Hhg + Cy^2 + 2KI;$$

but this mode of preparation is not advantageous, being attended with considerable loss.

Mercuric ethide is a transparent colourless liquid, having a faint ethereal odour, insoluble in *water*, sparingly soluble in *alcohol*, easily in *ether*. Specific gravity = 2·46. Boiling point 158° to 160° (Buckton); 159° (Frankland and Duppa). Vapour-density, obs. = 9·97; calc. (2 vol.) = 9·4.

Mercuric ethide burns with a smoky flame, giving off a large quantity of mercurial vapour. When poured into *chlorine gas*, it bursts into flame and is almost entirely destroyed. It acts violently also with *iodine* or *bromine*, forming mercuric iodethide or bromethide; if the action be conducted under water, ethyl, or its products of decomposition are eliminated: but if the liquid is kept cool by a freezing mixture, the nascent ethyl unites with the bromine;

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* In the preparation of mercuric amylide (p. 923), this intermediate distillation is not necessary, as the liquid retains sufficient fluidity to allow the action to complete itself.

$$\text{Hhg}(C^2H^5)^2 + Br^2 = \text{Hhg}C^2H^5Br + C^2H^5Br.$$

With excess of alcoholic *mercuric chloride*, it yields mercuric chlorethide (p. 923).

With *hydrochloric* or *sulphuric* acid, it yields hydride of ethyl and mercuric chlorethide or sulphatethide:

$$2\text{Hhg}(C^2H^5)^2 + H^2SO^4 = 2(C^2H^5.H) + \text{Hhg}^2\left\{\begin{matrix}(C^2H^5)^2\\SO^4\end{matrix}\right..$$

Sodium slowly decomposes mercuric ethyl, forming a bulky grey spongy mass, which is very liable to explode from slight causes, and instantly takes fire on coming in contact with the air. On applying a gentle heat, a violent evolution of gas takes place, consisting of ethyl and hydride of ethyl, sodium-ethyl being probably formed in the first instance, and then decomposed by the heat. (Buckton.)

Heated with excess of finely granulated *zinc* to 100° in a sealed tube, it yields zinc-ethyl and zinc-amalgam. Heated with *bismuth*, it yields in like manner bismuth-ethyl, but the decomposition is not complete. *Cadmium* heaetd with mercuric ethide to 100°–130°, becomes amalgamated, and forms a considerable quantity of cadmium-ethyl. *Gold* likewise become amalgamated, but forms no trace of an organo-metallic compound. Mercuric ethide is likewise decomposed when heated to about 150°, with *copper*, *iron*, or *silver*, the copper becoming slightly amalgamated, and inflammable gas being given off; but the decomposition appears to be due to the heat alone, independently of any specific action of the metal. No organo-metallic compound is formed in either case. (Frankland and Duppa.)

Mercuric Ethyl-hydrate. $\text{Hhg}''\left\{\begin{matrix}C^2H^5\\(HO)\end{matrix}\right.$. *Hydrate of Mercurethyl.*—Obtained by decomposing a boiling alcoholic solution of the chlorethide with oxide of silver, then filtering, distilling off the alcohol, and evaporating in vacuo. It then remains as a colourless oil, which is strongly alkaline and blisters the skin. It decomposes *ammonium-salts*, but not the salts of potassium or magnesium, and forms precipitates with the salts of *aluminium*, *zinc*, *tin*, *copper*, *gold*, and *platinum*. With a large excess of *sulphydric acid*, it forms a white precipitate which after a while turns yellow, brown, and black. With metallic *zinc* it forms zinc-ethyl, and amalgam of zinc. It dissolves in *acids*, forming crystallisable salts, viz. mercuric chlorethide, nitrethide, &c.

Mercuric Iodethide. $\text{Hhg}''(C^2H^5)I$.—This compound is obtained by the reactions above-mentioned (pp. 921, 922), or by mixing an alcoholic solution of the ethyl-hydrate with a slight excess of alcoholic iodine. It is insoluble in *water*, but soluble in boiling *alchohol* and *ether*, and separates on cooling in white shining laminæ. It dissolves also without decomposition in caustic *ammonia* and *potash*. It sublimes at 100° without decomposition, but requires a much stronger heat to melt it. It is decomposed by direct *sunshine*: hence in preparing it by the action of mercury on iodide of ethyl, the vessel must be exposed only to diffused daylight. (Dünhaupt, Strecker.)

Mercuric Nitrethide. $\text{Hhg}''\left\{\begin{matrix}C^2H^5\\NO^3\end{matrix}\right.$. *Nitrate of Mercurethyl.*—Nitrate of silver added to a solution of the iodethide, forms a precipitate of iodide of silver, and a solution of mercuric nitrethide, which yields colourless prisms by evaporation. (Strecker.)

Mercuric Phosphatethide, or *Phosphate of Mercurethyl*, is obtained by treating the chlorethide with phosphate of silver. It is very soluble in water, and remains on evaporation as a viscid diaphanous mass. (Dünhaupt.)

Mercuric Sulphatethide. $\overset{''}{\text{Hhg}}{}^2\left\{\begin{matrix}(C^2H^5)^2\\(SO^4)''\end{matrix}\right.$. *Sulphate of Mercurethyl.*—Prepared by decomposing the chlorethide with sulphate of silver. Crystallises from alcohol in shining laminæ.

Mercuric Sulphethide. $\overset{''}{\text{Hhg}}{}^2\left\{\begin{matrix}(C^2H^5)^2\\S\end{matrix}\right.$.—This compound separates as a yellowish-white pulverulent precipitate on adding sulphide of ammonium to an alcoholic solution of the chlorethide. It is very soluble in *alcohol*, *ether*, and *sulphide of ammonium*, and separates from the ethereal solution in the crystalline state, but always mixed with sulphide of mercury. The alcoholic solution is also decomposed by evaporation, depositing sulphide of mercury.

Methyl-compounds.

Mercuric Iodomethide. $\text{Hhg}''(CH^3)I$.—This compound was discovered by Frankland (Ann. Ch. Pharm. lxxxv. 380), who obtained it originally by the action of mercury on iodide of methyl in sunshine. In about a week, the liquid solidifies into a colourless crystalline mass, and by treating this mass with ether, the mercuric iodethide is dissolved, and may thus be separated from the remaining metallic mercury and the small quantity of iodide of mercury formed at the same time. Very little gas is given off during the reaction. Mercuric iodomethide is, however, more easily obtained by the action of iodine on an alcoholic solution of mercuric methide.

Mercuric iodomethide is a white solid body, insoluble in *water*, but dissolving pretty readily in common *alcohol*, more easily in *methylic alcohol*, and very easily in *ether* and in *iodide of methyl*. By spontaneous evaporation of either of these solutions, the iodide is obtained in small, nacreous, crystalline laminæ. At ordinary temperatures, it is slightly volatile, emitting a peculiar and unpleasant odour; the vapour when inhaled leaves a nauseous taste on the palate which lasts for several days. At 100°, the iodide is much more volatile, the crystals disappearing completely when exposed to a current of air at that temperature. At 143°, it melts and sublimes without decomposition, condensing in extremely thin, shining, crystalline laminæ.

Mercuric Methide. $Hhg''(CH^3)^2$. *Mercuromethyl. Hydrargomethyl.* Discovered by **Buckton** (Proc. Roy. Soc. ix. 91), who obtained it by distilling mercuric iodomethide with cyanide of potassium, hydrate of potassium, or lime. The best product is obtained with the cyanide. A mixture of this salt with mercuric iodomethide, after being well triturated in a mortar, is distilled by small portions over a lamp. Gaseous products are then evolved; iodide of potassium is formed; cyanogen is set free and remains in the form of paracyanogen; and mercuric methide passes over in the form of a heavy liquid, which may be purified by washing with water and rectification over chloride of calcium. The essential part of the reaction is represented by the equation:

$$2Hhg(CH^3)I \quad + \quad 2KCy \quad = \quad Hhg(CH^3)^2 \quad + \quad 2KI \quad + \quad Hhg \quad + \quad Cy^2.$$

Frankland and Duppa prepare mercuric methide by the action of sodium-amalgam on iodide of methyl, in presence of acetic ether. The mode of preparation is exactly the same as that already described (p. 925) for the preparation of mercuric ethide, a small Liebig's condenser being, however, attached to the neck of the flask, to arrest the vapour of iodide of methyl, which would otherwise be carried away by the escaping gas. At the end of the operation, the residues in the flasks are mixed with water and distilled in an oil-bath, the temperature of which need not be raised above 110°, and the ethereal distillate, after separation from the water which accompanies it, is agitated with alcoholic potash to remove acetic ether, and finally purified by washing with water.

Mercuric methide is a colourless, strongly refracting liquid, having a faint and somewhat mawkish taste. Specific gravity 3·069. Boiling point between 93° and 96°. Vapour density, obs. = 8·29; calc. = 7·97. It is insoluble in *water*, very soluble in *alcohol* and in *ether*, dissolves *phosphorus*, *caoutchouc*, and *resins* easily, *sulphur* in small quantity.

Mercuric methide is very inflammable and burns with a bright flame, giving off vapour of mercury. It does not unite directly with *oxygen*, *chlorine*, or other electronegative elements, but is completely decomposed by them. *Iodine* and *bromine* act upon it very energetically, eliminating methyl-gas and forming mercuric-, iodo-, or bromo-methide:

$$2Hhg(CH^3)^2 + I^2 \quad = \quad 2HhgCH^3I + (CH^3)^2.$$

It also forms mercuric iodomethide when heated with *mercuric iodide*.

With *stannic chloride* it forms a crystalline compound, which is decomposed by water, with formation of mercuric chloromethide and a soluble tin-salt. With strong *sulphuric* or *hydrochloric acid*, it acts like mercuric ethide (p. 925), giving off marsh-gas, and forming crystals of mercuric chloromethide or sulphatomethide. With *dilute acids* and metallic *zinc*, it yields metallic mercury and gaseous products; its salts (mercuric iodomethide, &c.) are decomposed in like manner (**Buckton**). Heated with metallic *zinc* alone, it yields zinc-ethyl and zinc-amalgam (**Frankland** and **Duppa**). With *trichloride of phosphorus*, it forms mercuric chloromethide.

Mercuric Nitromethide. $Hhg''\left\{\begin{matrix}CH^3\\NO^3\end{matrix}\right.$. *Nitrate of Hydrargomethyl.*—Obtained by treating an alcoholic solution of mercuric iodomethide with nitrate of silver, and evaporating the filtrate in vacuo. Crystallises in nacreous laminæ, containing $2Hhg(CH^3)NO^3.H^2O$, very soluble in *water*, sparingly in *alcohol*. At 100°, it melts to a colourless liquid which solidifies in a crystalline mass on cooling. Its solution is not precipitated by *potash* or *baryta-water*. *Hydrochloric acid* and soluble *chlorides* precipitate mercuric chloromethide in nacreous laminæ. (**Strecker**, Ann. Ch. Pharm. xcii. 79.)

Mercuric Oxymethide, or *Oxide of Hydrargomethyl*, is produced by the action of ammonia or the fixed alkalis on mercuric iodomethide. It is dissolved by an excess of either of these reagents, and the solutions yield with sulphide of ammonium a flocculent precipitate of the corresponding *sulphide*, having a faint yellowish colour, and a peculiar and most intolerable odour. (Frankland.)

MEROXENE. Syn. with Biotite. (See MICA.)

MESACONIC ACID. $C^5H^6O^4$. *Citracartic acid* (Gottlieb, Ann. Ch. Pharm. lxxvii. 268; Pebal, *ibid.* lxxviii. 129; Baup, *ibid.* lxxxi. 96).—An acid obtained by boiling a weak solution of citraconic acid for half an hour with about the sixth of its volume of nitric acid. The reaction takes place quietly, and on cooling the acid is deposited in a porcelain-like mass. A certain quantity of a nitro-compound is produced at the same time, from which the acid may be purified by treatment with animal charcoal.

Mesaconic acid forms a mass of fine lustrous needles, difficultly soluble in cold, but readily so in hot *water*, and also in *alcohol* and in *ether*. It melts at 200° to a clear liquid, which solidifies to a crystalline mass. It reddens litmus and decomposes carbonates. Heated with concentrated *hydriodic acid* to 140°—160°, it separates iodine and forms pyrotartaric acid; it is also converted into this acid by *sodium-amalgam*. With *bromine*, at 60°—80°, it forms mesodibromo-pyrotartaric acid, $C^5H^6Br^2O^4$. (Kekulé, Ann. Ch. Pharm. Suppl. ii. 85.)

Mesaconic acid is dibasic, its salts having the formulæ $C^5H^4M^2O^4$ and $C^5H^5MO^4$. They are almost all crystallisable.

The *neutral barium-salt*, $C^5H^4Ba^2O^4.4H^2O$, is obtained by saturating the acid with carbonate of barium. It forms monoclinic prisms, which are unalterable in the air, and give off the greater part of their water of crystallisation at 100°. The *acid barium-salt*, $C^5H^5BaO^4.H^2O$, forms hexagonal plates of a pearly lustre, which persistently retain an excess of acid, from which they are freed with difficulty. The *neutral calcium-salt*, $C^5H^4Ca^2O^4.H^2O$, forms small agglomerated needles soluble in 16 pts. of water. The *neutral silver-salt* is a crystalline precipitate, difficultly soluble in water. The *acid silver-salt*, $C^5H^5AgO^4$, is obtained in needles by dissolving the neutral salt in solution of mesaconic acid and evaporating. E. A.

MESACONIC ETHER. $C^9H^{14}O^4 = C^5H^4(C^2H^5)^2O^4$. Obtained by distilling a mixture of mesaconic acid, sulphuric acid, and alcohol. It is a colourless mobile liquid, with an agreeable fruity odour and bitter taste. Its density is 1·043, and it distils at 220° without alteration. It is not attacked by ammonia. Boiled with baryta-water it yields alcohol and mesaconate of barium. E. A.

MESITE. An oxygenated oil, very mobile, boiling above 70°, and soluble in 3 pts. of water, said to be obtained by distilling lignone with sulphuric acid. (Wiedemann and Schweizer.)

MESITENE. Another very mobile oil, boiling at 63°, and soluble in 3 pts. of water, obtained in like manner.

MESITIC ALCOHOL. A name given to acetone, on the supposition that it is an alcohol containing the radicle *mesityl*, C^3H^5, isomeric with allyl.

MESITIC ALDEHYDE. C^3H^4O. A body isomeric with acrolein, produced, together with trinitromesitylene, by heating acetone with half its bulk of strong nitric acid. The action is extremely violent, so that it is necessary to cool the vessel as soon as effervescence begins, then heat it again and repeat this treatment several times. When the action is completed, an oil separates, consisting of mesitic aldehyde mixed with trinitromesitylene.

Mesitic aldehyde is lighter than water, has a sweet pungent odour, is very slightly soluble in water, but dissolves instantly in caustic potash, yielding a yellowish-brown liquid. It absorbs ammonia gas with great avidity, forming a brown resinous mass, which dissolves in water, the solution yielding by spontaneous evaporation crystals of *mesitic aldehyde-ammonia*. Nitrate of silver added to the solution of these crystals, forms a yellow precipitate, which blackens when heated; the reduction is accelerated by the addition of a few drops of potash. (Kane, Pogg. Ann. xli. 491.)

MESITIC CHLORAL. Syn. with Dichloracetone. (See ACETONE, i. 30.)

MESITIC ETHER. Syn. with Oxide of Mesityl. (See MESITYL.)

MESITIN-SPAR. $(Mg;Fe)^2CO^3$ or $(Mmg;Ffe)CO^3$. *Breunnerite, Pistomesite.*—This mineral occurs in rhombohedral crystals isomorphous with spathic iron ore and magnesite. $R : R = 107° 23'$; $oR : R = 136° 52'$. Length of principal axis $= 0·81135$. Observed planes, R, $-\frac{1}{2}$ R. Cleavage rhombohedral, perfect. Crystals often imbedded. Also massive, granular, and fibrous. Hardness = 4 to 4·5. Specific gravity = 3 to 3·63. Colourless, whitish, yellowish, and often brown on exposure. Transparent to subtranslucent. Brittle. The mineral may be regarded as a mixture of the isomorphous carbonates $MmgCO^3$ and $FfeCO^3$, the proportion of the former varying from 89·7 to 42·7 per cent., and that of the latter from 5·1 to 57·2 per cent. Some specimens also contain small quantities of calcium and manganese. Mesitinspar occurs in chlorite slate at St. Gothard; also in the Zillerthal; at Hall, and elsewhere in the Tyrol, and at Traversella in Piedmont. The species includes much of the so-called *brown spar*. (Dana, ii. 443.)

MESITYL. A hypothetical monatomic radicle, supposed by Kane to exist in acetone (regarded as $\left.\begin{matrix}C^3H^5\\H\end{matrix}\right\}O$), and in certain products obtained from it.

Chloride of Mesityl, C^3H^5Cl, is produced by passing hydrochloric acid into acetone, which absorbs it in large quantity; or better by adding 2 pts. of pentachloride of phosphorus, by small portions, to 1 pt. of acetone, properly cooled, then adding water, which separates the chloride of mesityl in the form of an oily liquid heavier than water. It is resolved by heat into hydrochloric acid and mesitylene Alcoholic potash converts it into oxide of mesityl. (Kane, Pogg. Ann. xliv. 476).

Hydrate of Mesityl. $\left.\begin{matrix}C^3H^5\\H\end{matrix}\right\}O$. Syn. with Acetone.

Iodide of Mesityl. Oily liquid insoluble in water, obtained by distilling acetone with iodine and phosphorus. It has not been analysed. (Kane.)

Oxide of Mesityl or *Mesitic ether.* $(C^3H^5)^2O$.—Produced: 1. By the action of alcoholic potash in excess on chloride of mesityl.—2. Together with many other products, by the action of strong sulphuric acid on acetone (Kane).—3. By the action of lime on acetone. Acetone left for several weeks in contact with quicklime, and then subjected to fractional distillation, yields, between 100° and 250°, a mixture of oxide of mesityl, boiling at about 129°, and phorone, $C^9H^{14}O$, boiling at 290°, which may easily be separated by rectification. (Fittig, Ann. Ch. Pharm. cx. 23.)

Pure oxide of mesityl is a colourless oil, smelling like peppermint. Specific gravity 0·848 at 23°. Boiling point (corrected) 131°. Vapour-density, obs. = 3·67; calc. 3·39 (Fittig). It burns with a very bright flame (Kane). It is insoluble in *water*, mixes in all proportions with *alcohol* and *ether*; is converted by *nitric acid* into a brown resinous mass, and by *chorine* into a heavy oil, which appears to have the composition $C^6H^8Cl^2O$. (Fittig.)

Mesityl-hypophosphorous acid.—An acid contained, according to Kane, in the syrupy residue obtained by distilling acetone with iodine and phosphorus. This residue solidifies, on cooling, to an amaranthine mass, and yields, by saturation with carbonate of barium, a salt containg 20·0 per cent, carbon, 3·8 hydrogen, and 43·8 baryta, whence Kane deduces the formula $PBaO.C^3H^6O$ (calc. 20·7 carbon, 3·45 hydrogen, and 44·02 baryta).

Mesityl-phosphoric acid.—An acid produced by treating acetone with phosphoric acid. The resulting liquid neutralised with bases, yields soluble salts. The *sodium-salt* forms small rhomboïdal laminæ, which, when exposed to the air, become opaque, and give off part of their water. When heated, they melt in their water of crystallisation, and ultimately leave a white mass, which, at a higher temperature, swells, blackens, and burns, leaving phosphate of sodium. The salt was found to contain 48·8 per cent. sodic phosphate, and 29·0 water, agreeing approximately with the formula $PNaO^4.C^3H^6O.\frac{5}{2}H^2O$, which requires 49·9 sodic phosphate, and 28·21 water. (Kane.)

Mesitylo-sulphuric acids.—Kane found, among the products of the action of sulphuric acid upon acetone, two acids analogous in composition to ethyl-sulphuric acid.

1. When acetone is mixed with twice its volume of strong sulphuric acid, the liquid becomes very hot, assumes a dark brown colour, and gives off a large quantity of sulphurous anhydride; and if it be mixed after cooling with 2 or 3 volumes of water and neutralised with chalk, a deliquescent mass is obtained, in which small prisms may be distinguished, yielding, according to Kane's analysis, 70·5 per cent. calcic sulphate, 18·5 carbon, 3·3 hydrogen, and 7·9 oxygen, numbers which Kane represents by the formula $C^3H^6O.Ca^2SO^4$.

2. By treating 2 vol. acetone with 1 vol. sulphuric acid, and diluting with water when cold, Kane obtained another acid, the calcium-salt of which was found to contain 23·7 per cent. lime, 30·3 carbon, and 4·4 hydrogen, and may be represented, according to Kane, by the formula $2C^3H^6O.Ca^2SO^4$.

Gerhardt made several attempts to obtain these acids by the processes above described, but did not obtain a trace of either of them; he considers it probable that the only acid produced by the action of oil of vitriol on acetone is methyl-sulphuric acid. (*Traité*, i. 704.)

MESITYLENE or **MESITYLOL.** C^9H^{12}. (Kane, Pogg. Ann. xl. iv. 474.—Hofmann, Chem. Soc. J. ii. 104.—Cahours, Compt. rend. xxiv. 255; Chem. Soc. J. iii. xvii.)—A hydrocarbon, isomeric with cumene, produced by the action of sulphuric acid upon acetone. To prepare it, 2 vol. acetone are distilled with 1 vol. strong sulphuric acid, the heat being carefully regulated. Two layers of liquid then collect in the receiver, the upper consisting of very impure mesitylene, and the lower containing sulphurous and acetic acids, resulting from a secondary decomposition. The upper layer is rectified, first over the water-bath to separate undecomposed acetone, and then over the naked fire. But the product thus obtained does not exhibit a constant boiling point, and requires to be purified by numerous rectifications (Hofmann), and final distillation over phosphoric acid. (Cahours.)

Mesitylene is a very light, colourless substance, having a slight alliaceous odour. It boils between 155° and 160° (Hofmann), between 162° and 164° (Cahours). Vapour-density, obs. = 4·345 to 4·282 (Cahours); calc. = 4·160.

Mesitylene burns with a bright, but very smoky flame. It dissolves *iodine*, forming a dark brown liquid which is not altered by exposure to sunshine. With *bromine* and *chlorine*, it forms crystalline substitution-products. Boiling *nitric* acid converts it into mesitic aldehyde (Kane). A mixture of *fuming nitric* and *fuming sulphuric acids* converts it immediately, and without rise of temperature, into trinitromesitylene (Cahours). It is likewise decomposed by strong sulphuric acid, but not by aqueous alkalis (Kane). Fuming sulphuric acid converts it into mesitylene-sulphuric acid $C^9H^{12}SO^3$. (Cahours.)

Derivatives of Mesitylene.

Tribromomesitylene. $C^9H^9Br^3$.—When bromine is added drop by drop to mesitylene, waiting each time till the heat evolved has subsided, and taking care to keep the mesitylene in excess, a white crystalline compound is formed, which may be freed from hydrobromic acid by washing with water, in which it is perfectly insoluble. Two or three crystallisations from boiling alcohol render it absolutely pure. It forms white needles, which volatilise without decomposition, and are not changed by boiling with potash or ammonia. (Hofmann.)

Trichloromesitylene. $C^9H^9Cl^3$.—To prepare this compound, chlorine gas is passed through mesitylene till the liquid solidifies in an acicular mass, which is then dissolved in hot ether and crystallised by cooling, the undecomposed mesitylene remaining in the mother-liquid. The product is purified by recrystallisation, and the crystals dried between paper, but not in contact with the air.

It forms white, shining, four-sided prisms, resembling sulphate of quinine, volatilising only at a strong heat, but without decomposition. They may also be sublimed without alteration in dry ammoniacal gas, and are not decomposed by alcoholic potash. (Kane.)

Nitromesitylene. $C^9H^{11}NO^2$.—Formed by treating mesitylene with fuming nitric acid, not in excess, and carefully cooling the mixture during the action. This compound, when treated with an alcoholic solution of potash, becomes heated and evolves two products on distillation. One of these is a liquid, which is produced in very small quantity only, and exhibits the properties of an alkaloid; the other, which is solid, dissolves very readily in alcohol, and separates from it by spontaneous evaporation in very fine tabular crystals; it is isomeric with nitromesitylene. (Cahours.)

Dinitromesitylene. $C^9H^{10}(NO^2)^2$.—Obtained by boiling mesitylene with moderately strong nitric acid. After a few distillations, the whole of the mesitylene is converted into a crystalline compound, which may be purified by washing with water and recrystallisation from alcohol. With dilute nitric acid a less definite result is obtained, the mesitylene being converted, after repeated distillation, into a yellow oil, which shows a tendency to crystallise, but appears to be a mixture.

This compound crystallises in fine needles, often several inches long, and in appearance resembling those of trinitromesitylene (*vid. inf.*). It volatilises without decomposition, and dissolves with great facility in alcohol. (Hofmann.)

Nitromesidine. $C^9H^{12}N^2O^2 = C^9H^{12}(NO^2)N$. (Maule, Chem. Soc. Qu. J. ii. 116.)—A base obtained by the action of sulphydric acid on dinitromesitylene:

$$C^9H^{10}N^2O^4 + 3H^2S = C^9H^{12}N^2O^2 + 2H^2O + S^3.$$

When an alcoholic solution of dinitromesitylene is submitted to the action of sulphydric acid, the liquid assumes a dark colour and deposits gradually a large quantity of sulphur, the odour of the sulphydric acid being at the same time destroyed. This treatment is continued for several days, till the sulphydric acid is no longer decomposed. On the addition of hydrochloric acid, sulphur is again precipitated, and on separating this by filtration, a clear liquid is obtained, which when mixed with potash

MESOXALIC ACID. $C^3H^2O^5$. (Liebig and Wöhler, Ann. Ch. Pharm. xxvi. 298.—Svanberg, Berz. Jahresb. xxvii. 165.)—An acid formed when alloxan or alloxanic acid is boiled with aqueous alkalis, urea being simultaneously produced:

$$\underset{\text{Alloxanic acid.}}{C^4H^4N^2O^5} + H^2O = \underset{\text{Mesoxalic acid.}}{C^3H^2O^5} + \underset{\text{Urea.}}{CH^4N^2O}.$$

The acid is obtained by decomposing the barium-salt by sulphuric acid, or the lead-salt by sulphydric acid. It is crystallisable, and has a very sour taste, and a strong acid reaction. It is very soluble in water, and its solution is not decomposed by boiling. Its aqueous solution, when neutralised with ammonia, gives with salts of barium, strontium, and calcium, white precipitates, soluble in acids, or in a large quantity of water.

Mesoxalic acid is dibasic. The *barium-salt*, $C^3Ba^2O^5$, is prepared by boiling a hot saturated solution of alloxanate of barium: a mixture of alloxanate, mesoxalate, and carbonate is precipitated, and the solution yields, on evaporation, crystalline crusts of urea and mesoxalate of barium, the latter of which is removed by washing with alcohol. The salt forms yellow laminæ, which are anhydrous at 90°, and at 100° are partially decomposed. Liebig and Wöhler found 55·93 per cent. barium in the salt; the calculated percentage is 56·49. The *calcium-salt* forms thin tables, which at 90° contain 2 at. water; at 140° they lose 1 at. water, and above that temperature are decomposed. It is much more soluble than the barium-salt (Svanberg). The *lead-salt*, obtained by dropping aqueous alloxan or alloxanic acid into a boiling solution of neutral acetate of lead, appears to be a basic salt, containing 4 at. lead. It is decomposed when gently heated in the air, pure oxide of lead remaining; hot nitric acid converts it into oxalate of lead. According to Liebig and Wöhler, the normal lead-salt is formed by adding mesoxalic acid to neutral acetate of lead. The *silver-salt* is obtained as a yellow precipitate when mesoxalic acid and ammonia are added to nitrate of silver: it is probably a basic salt, as it is entirely decomposed by heat into carbonic anhydride and metallic silver, perhaps thus, $C^3Ag^2O^5 + Ag^2O = 3CO^2 + Ag^4$. (Liebig and Wöhler.)

When mesoxalic acid is compared with carbonic and oxalic acids, it will be seen that the three acids may be regarded as containing respectively the diatomic radicles carbonyl CO, oxalyl C^2O^2, and mesoxalyl C^3O^3.

Carbonic acid	CH^2O^3	$= CO.H^2.O^2$.
Oxalic acid	$C^2H^2O^4$	$= C^2O^2.H^2.O^2$.
Mesoxalic acid	$C^3H^2O^5$	$= C^3O^3.H^2.O^2$.

The decomposition of oxaluric and alloxanic acids into urea, oxalic, and mesoxalic acids, respectively, shows that alloxanic bears to oxaluric acid the same relation that mesoxalic does to oxalic acid, and from this point of view alloxanic acid may be regarded as mesoxaluric acid. A similar relation is evident between alloxan and parabanic acid. F. T. C.

MESUA FERREA. This plant, which grows in India, yields a fixed oil having a density of 0·954, a chestnut-brown colour, and solidifying at + 5. (Lepine, J. Pharm. [3] xl. 16.)

METACETAMIDE. Syn. with PROPIONAMIDE.

METACETIC ACID. Syn. with PROPIONIC ACID.

METACETONE. $C^6H^{10}O$? (Frémy, Ann. Ch. Phys. [2] lix. 6.—Gottlieb, Ann. Ch. Pharm. lii. 127.)—A substance occurring among the products of the dry distillation of sugar, starch, gum or mannite, with lime; it has also been obtained by the distillation of lactate of calcium, and occurs among the volatile oils formed by the distillation of wood.

Frémy prepares metacetone by gently heating an intimate mixture of at least 500 grms. of sugar with 8 times its weight of quicklime in a capacious retort, withdrawing the fire after a while, because the water disengaged from the sugar, coming in contact with the lime, raises the temperature high enough to complete the reaction without further application of external heat. If the mixture has been well made, scarcely any inflammable gas is evolved, and a complex oil passes over into the receiver. This oil is shaken up with water to remove the acetone which it contains, and the residue, which floats on water, is rectified till it exhibits a constant boiling point. It is difficult, however, to obtain a pure product. According to Gottlieb, it is best to use only 3 pts. lime to 1 pt. sugar, and to keep the receiver cool. Metacetone is obtained in the same manner from starch, which indeed appears to yield rather more metacetone than acetone: gum, on the contrary, yields a comparatively larger quantity of acetone.

Metacetone is a colourless oil, having an agreeable odour, insoluble in *water*, very soluble in *alcohol* and *ether*. Boiling point 84°. It contains, according to the mean of Frémy's analyses, 72·2 per cent. carbon, and 10·1 hydrogen. The formula $C^6H^{10}O$, which represents it as isomeric with oxide of mesityl and oxide of allyl, requires 73·5 carbon, 10·2 hydrogen, and 16·3 oxygen. When distilled with *acid chromate of potassium* and strong *sulphuric acid*, it yields carbonic anhydride, acetic acid, and propionic acid. As these products are the same as those obtained by the oxidation of propione, metacetone is sometimes regarded as impure propione (Gm. ix. 409). (Pure propione, $C^5H^{10}O$, obtained by distillation of propionate of barium, boils at 84° and contains 69·3 carbon, and 11·8 hydrogen.) Metacetone dropped on heated *potash-lime* or fused *hydrate of potassium* distils over in great part unaltered, the residue containing only traces of propionic acid. (Gottlieb.)

METACETONIC ACID. Syn. with PROPIONIC ACID.

METACETONITRILE. Syn. with PROPIONITRILE OF CYANIDE OF ETHYL (ii. 211).

METACHLORITE. A foliated columnar mineral from the Büchenberg near Elbingerode in the Harz. It has a vitreous to pearly lustre and dull leek-green colour. Hardness = 2·5. Gelatinises with acids. Contains, according to List, 23·77 per cent. silica, 16·43 alumina, 40·36 ferric oxide, 3·10 magnesia, 0·74 lime, 1·37 potash, 0·08 soda, and 13·75 water (= 99·60), whence the formula $3(3M^2O.SiO^2).2(Al^4O^3.SiO^2).10H^2O$ or $4(M^2O.SiO^2).3M^2O.2Al^4O^3).8H^2O$. (*Rammelsberg's Mineralchemie*, p. 541.)

METACHROMIC OXIDE. See CHROMIUM, OXIDES OF (i. 949).

METACINNAMEIN. See CINNAMEIN (i. 980).

METACROLEIN. See ACROLEIN (i. 57).

METAFERRIC OXIDE. The modification of ferric hydrate obtained by Péan de St. Gilles by boiling the ordinary yellow hydrate in water (p. 395).

METAFURFUROL. See FURFUROL (ii. 752).

METAGALLIC ACID. See GALLIC ACID (ii. 760).

METAHUMIC ACID. See ULMIC ACID.

METAL. *Metall. Métal.* **METALLOÏD.** *Metalloïd. Métalloïde.* The term metal has long been commonly applied, in technical and popular language, to a number of substances which agree in presenting, in various degrees, a combination of certain well-defined physical characters, by which many of them are easily distinguishable from most other substances. Gold and silver were formerly regarded as the typical representatives of this class of substances. These characters, however, are not by any means absolutely distinctive of metals; for there are many substances which are not metallic, and which nevertheless possess in a high degree some of the physical characters of metals. At a very early date, attempts made by Basil Valentine (*Conclusiones*), Paracelsus (1539), and Boerhave (1732), to adopt a system of classification, which would separate the more characteristic metals from substances possessing certain metallic characters, such as zinc, antimony, bismuth, antimony-glance, pyrites and galena, which were termed semi-metals or bastard metals. In 1735, Brandt proposed to make the presence or absence of malleability the principle of this classification, and upon this ground he separated mercury from the metals. The same view was adopted by Vogel (1755, *Institutionibus Chemiæ*) and Buffon (1785, *Histoire naturelle des Minéraux*). Subsequently, when Braune had observed the solidification of mercury by cold in 1759–60, and this had been confirmed by Hutchins and Cavendish in 1783, the malleability of this substance became known, and it was classed among the metals.

The insufficiency of the distinction which had been drawn between metals and semi-metals was pointed out by Fourcroy (1789, *Eleméns d'Histoire Naturelle et de Chemie*, ii. 380) as being evident from the fact that "between the extreme malleability of gold and the singular fragility of arsenic, other metals presented only imperceptible gradations of this character, and because there was probably no greater difference between the malleability of gold and that of lead, which was considered to be a metal, than there was between lead and zinc, which was classed among semi-metals, while in the substances intermediate between zinc and arsenic the differences were slight."

The distinction between metals and semi-metals was soon afterwards abandoned, and at the time when the existing system of chemistry was established by Lavoisier, the class Metal comprised seventeen substances. Their chemical relations were then little known, and they were classified together as metals, chiefly on account of their analogy in physical characters, and because they were regarded as chemically simple or elementary substances. Since that time a great number of other simple substances have been discovered, which possess more or less the physical characters of metals, but which do not possess them in that degree which was formerly considered to be the distinctive peculiarity of a metal.

tained as to their metallic nature, and it was proposed to distinguish them from metals, on account of their peculiar physical characters, and to term them *metalloïds*,* as possessing only some resemblance to metals (Erman and Simon, 1808, *Gilbert's Annalen*, xxviii. 121). This proposal was not adopted, and in 1811 Berzelius applied the term *metalloïd* to distinguish the non-metallic elementary substances from the metals, in which sense it has been commonly used up to the present time, chiefly in relation to substances which, like the metals, have not been resolved into separate constituents, and which are consequently regarded as elementary.

A high degree of density was long considered to be a peculiarly distinctive character of metallic substances; but the discovery of the earthy and alkaline metals showed that this is not the case, and that, in regard to this, as well as other physical characters, the term metal has only a relative application, and should not be considered as representing a class of substances entirely distinct from those termed metalloïds.

This fact has been rendered still more apparent by the advanced investigation of the chemical characters and relations of metals and other substances; for while some of the substances possessing, in a marked degree, certain of the physical characters, hitherto regarded as distinguishing metals, do not possess, in an equal degree, the chemical characters of metals, there are, on the contrary, substances possessing few or none of the physical characters of metals, but manifesting in their chemical characters and relations the most marked analogy with well-defined metals. Thus for instance antimony, molybdenum, arsenic, titanium, &c., form compounds with oxygen, sulphur, &c., which are the analogues of sulphuric, phosphoric, nitric, and silicic acids; while, on the other hand, the electropositive constituents of the earths and alkalis, also hydrogen, ammonium, and some of the hydrocarbon radicles, correspond closely with the electropositive metals, in their general chemical functions, and form with oxygen and sulphur, &c., compounds which are in the highest degree analogous to the basic compounds of silver, lead, iron, &c., with oxygen.

In a strictly chemical sense, therefore, the term metal must be regarded as representing an ideal type, to which a number of substances approximate more or less, independently of their physical characters and of their simple or compound nature.

The elementary substances generally regarded as metallic are mostly solid at the ordinary temperature, the only exception being mercury (p. 933). With the exception of arsenic, they are all capable of becoming liquid at various temperatures peculiar to each, and some of them are capable of being converted into vapour by heat. In the solid and compact state they are in a high degree impervious to light. A mass of metal is absolutely opaque; but very thin laminæ of some metals allow certain rays to penetrate through them, as for instance gold-leaf, which transmits light of a green colour. (Faraday, see pp. 636, 642.)

In consequence of this impermeability by light and the accompanying high reflective power of metals in the compact or liquid states, they possess a peculiar lustre or brilliancy, which may be developed by polishing their surfaces. The colour of most metals is a peculiar grey, with a varying tint of blue; but some few are yellow or red, as gold and copper, brass, bronze, &c. (see LIGHT, p. 641 *et seq.*), the colour being due to an unequal power of absorption for different rays, and varying according to the angle which the incident rays form with the surface of the metal. When this angle is very small, the whole of the rays are reflected, and all metals appear quite colourless.

One of the characters which, in combination with those already mentioned, has been regarded as most distinctive of metallic substances, is an internal mobility, in virtue of which the shape of a mass of metal may be altered by pressure, hammering, or by other mechanical means, without disintegration or disruption of the mass. This character, which is presented in various degrees and modes by different metals, is expressed by the terms *malleability*—denoting the capability of flattening or spreading out under the hammer, or between rollers—and *ductility*—denoting the capability of becoming longer and thinner by drawing through a hole of less area than the transverse section of the piece of metal.

For individual metallic substances, the degrees of malleability and ductility are by no means equal; many metals, which are in a high degree malleable, as tin and lead, cannot be drawn into very fine wire, while others which are less malleable, as iron, copper, gold, possess far greater ductility. Both characters are considerably influenced by temperature. Within certain limits they are generally greater at high than at low temperatures. The mechanical working of a metal is also productive of an alteration in its molecular condition, attended with diminution of malleability and ductility (*hammer-hardened; écroui*). In such cases those characters may be restored to the metal by heating it and allowing it to cool slowly (*annealing; anlassen; recuire*).

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* From *μέταλλον*, metal, and *εἶδος*, likeness.

Some metals possess so little malleability or ductility that they cannot be rolled into sheets, or drawn into wire.

Tenacity, or the resistance to forces which tend to tear asunder, either by tension, crushing, or wrenching, is another character which metals possess in very unequal degrees. It is intimately connected with molecular condition, and is in some way related to malleability and ductility. It is largely influenced in particular metals by the presence or absence of certain admixtures; by the manner in which they have been worked into shape, and by temperature. In general it is reduced by increase of temperature; but in some cases it is increased within a certain limited range of temperature, as in the case of iron (see COHESION, i. 1078). Some metals possess but a very slight degree of tenacity, and are then termed brittle—as zinc, antimony, and arsenic.

Elasticity, or the capability of a bar of metal to recover its original shape and dimensions, after being bent or stretched, is also a character connected with tenacity and internal mobility. It varies much in different metals.

Metallic substances differ very widely in the degree of *hardness* they possess, or are capable of acquiring by sudden cooling or otherwise. Some are so soft as to admit of being kneaded like wax (potassium and sodium), others are capable of scratching quartz or even diamond (steel, chromium). The presence of small amounts of various substances, such as carbon, silicon, &c., in metals, often communicates to them considerable hardness. As a general rule, a metal is more brittle in proportion to its degree of hardness.

Metals are capable of assuming a *crystalline structure*, generally belonging to the cube, octahedron, or some other form of the regular system; antimony and arsenic crystallise in rhombohedrons. Metals occurring native are frequently crystallised. The existence of crystalline structure in a metal, considerably influences its tenacity. It is generally accompanied by an increased degree of brittleness, and those metals which are most easily crystallised are, as a general rule, the most brittle. Crystalline structure is sometimes assumed by metals, while in the solid state, under the influence of long continued heat, of percussion or of vibration, and other mechanical actions, and the change thus induced is often of importance in relation to technical applications (see IRON, *ante*, p. 327). Metals may often be crystallised by slowly cooling them in a melted state, and when partly solidified, pouring off the remaining liquid metal (see BISMUTH, i. 590; LEAD, iii. 478). Metals often assume a crystalline structure when slowly deposited from solutions of their saline compounds, and some can be crystallised by sublimation (zinc, arsenic).

Metals and metalloïds in general present a marked difference in their power of conducting electricity and heat; the conductivity of metals for electricity is greater than that of any other substances. It varies considerably in different metals, and to some extent in the individual metals, according to their molecular condition, temperature, and the presence or absence of foreign admixtures.* The purer and softer the metal, the greater its conductivity: the higher the temperature of the metal, the less its conductivity. The conductivity of some metalloïds is increased by elevation of temperature. (See Wiedemann, *Lehre vom Galvanismus und Electromagnetismus*, i. 180.—Matthiessen, 1856, Proc. Roy. Soc. xi. 516.)

Metals and metalloïds differ in their electrical relations, the former being, as a class, electro-positive, the latter electro-negative. The distinction, however, is only one of degree, and metals present similar differences among each other. (See ELECTRICITY, ii. 432.)

Metals differ widely in their capacity for heat. The specific heat of sodium amounts to nearly ten-fold that of bismuth, lead, mercury, or gold. The conductivity for heat also differs greatly, though metals generally possess a comparatively high degree of conductivity for heat. (See Despretz, Compt. rend. xxxv. 540.—Wiedemann and Franz, 1854, Ann. Ch. Phys. xli. 107.)

The following table presents some of the principal physical characters of the best known elementary metals and metalloïds, so far as they have been determined. In some cases the numbers given are only approximative. It must also be remembered that the existence of these characters, and the degrees in which they are presented by particular substances, are sometimes due to the molecular condition of the substance, rather than to any inherent peculiarity. This is more especially known to be the case with the metalloïds, several of which are polymorphic, as sulphur, phosphorus, carbon, boron, silicon, &c. (See DIMORPHISM, ii. 331.)

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* The values given in the accompanying table are taken from Matthiessen's experiments (Phil. Trans. 1864, p. 199, Phil. Mag. [4] xiii. 81). The letters *h*, *p*, and *s* prefixed to the numbers in column 6, indicate that the wires were *hard-drawn*, *pressed*, or *soft*.

Discovered by	in		Specific gravity.		Specific heat.	Melting point.	Conductivity for	
			Water=1	Air=1			Heat.	Electricity at 0° C.
Wood	1741	**Platinum**	21·50	. .	0·0324	. .	8·4	a. 18·03
Descotils: Tennant	1803	**Iridium**	21·15	. .	0·0326			
		Gold	19·26	. .	0·0324	1200° ?	53·2	h. 77·96
								s. 79·33
Klaproth	1789	**Uranium**	18·40	. .	0·0619			
d'Elhujar	1783	**Tungsten**	18·30	. .	0·0334			
		Mercury	15·60	. .	0·0319	—39°		
		liquid	13·60	. .	0·0333	. .	. .	1·656
Crookes: Lamy	1862	**Thallium**	11·90	. .	0·0336	. .	. .	p. 9·16
Wollaston	1803	**Palladium**	11·80	. .	0·0593	. .	6·3	s. 18·44
		Lead	11·33	. .	0·0314	332°	8·5	p. 8·32
Wollaston	1803	**Rhodium**	11·00	. .	0·0553			
		Silver	10·57	. .	0·0570	1000° ?	100	h. 100
								s. 108·57
S. Tennant	1803	**Osmium**		. .	0 0311			
		Bismuth	9·80	. .	0·0308	270°	1·8	p. 1·24
		Copper	8·94	. .	0·0952	1200° ?	73·5	h. 99·95
								s. 102·21
Cronstedt	1751	**Nickel**	8·82	. .	0·1086	. .	. .	s. 13·11
Hjelm	1782	**Molybdenum**	8·63	. .	0·0722			
Brandt	1733	**Cobalt**	8·51	. .	0·1070	. .	. .	s. 17·22
Stromeyer	1818	**Cadmium**	8·45	. .	0·0567	320°	. .	p. 23·72
Gahn: Scheele	1774	**Manganese**	8·02	. .	0·1217			
		Iron	7·84	. .	0·1138	2000° ?	11·9	s. 16·81
		Tin	7·30	. .	0·0562	. .	14·5	p. 12·36
		Zinc	7·13	. .	0·0955	433°	. .	p. 29·02
Vauquelin	1797	**Chromium**	7·01					
		Antimony	6·72	. .	0·0508	450°	. .	p. 4·62
Gregor	1791	**Titanium**						
Brandt	1733	**Arsenic**	5·63	10·40	0·0814	. .	. .	p. 4·76
Davy	1807	**Barium**	4·00	. .	. .	450°		
Wöhler	1828	**Aluminium**	2·56	. .	0·2143	.	. .	s. 56·06
Davy	1807	**Strontium**	2·54	. .	. .	. .	. .	p. 6·71
Wöhler	1828	**Glucinum**	2·10					
Bussy	1829	**Magnesium**	1·74	. .	0·2499	433°	. .	s. 41·17
Davy	1807	**Calcium**	1·58	. .	. .	. .	. .	p. 22·14
Bunsen	1860	**Rubidium**	1·52					
Davy	1807	**Sodium**	0·97	. .	0·2934	90°	. .	p. 40·52
„	„	**Potassium**	0·86	. .	0·1696	55°	. .	p. 22·62
Mosander	1839	**Lanthanum**	0·83					
Arfwedson	1818	**Lithium**	0·59	. .	0·9408	. .	. .	p. 19·00
		Hydrogen	. .	0·0691	3·4090			
Rutherford		**Nitrogen**	. .	0·9713	0·2438			
Priestley	1774	**Oxygen**	. .	1·1056	0·2175			
Scheele	1774	**Chlorine**	. .	2·47	0·1210			
		liquid	1·33					
Brandt	1769	**Phosphorus**	1·84	4·42	0·1887			
		red	1·96	. .	0·1700			
		Sulphur	1·98	6·62	0·1776			
		trimetric	2·07					
		Carbon	2·27	. .	0·2008			
		crystalline	3·53	. .	0·1469			
Gay-Lussac Thénard Davy	1808	**Boron**	2·63	. .	0·2500			
Berzelius	1810	**Silicon**	2·34	. .	0·1750			
		crystalline	2·49	. .	0·1774			
Balard	1826	**Bromine**	3	5·54	0·0555	—12°		
		liquid	3·19					
Berzelius	1817	**Selenium**	4·28	8·20	0·0744			
			4·80					
Courtois	1811	**Iodine**	4·95	8·72	0·0541			
Müller	1782	**Tellurium**	6·24	. .	0·0474	. .	. .	0·0008

Only a few metals occur native, viz. gold, platinum, palladium, iridium, and rhodium, which are almost always found in the metallic state—silver, copper, mercury, bismuth, arsenic, which are often found in the metallic state—iron, antimony, lead? zinc? which are very rarely found in that state.

For the most part, metals occur naturally as constituents of various minerals, in which they are combined with oxygen, sulphur, chlorine, or arsenic, &c., in various proportions and modes.

Of the metalloïds only three occur native to any considerable extent, viz. nitrogen, oxygen, and sulphur. Carbon and selenium occur but rarely in an isolated state. It is doubtful whether fluorine has yet been obtained in the free state, even artificially (see ii. 673).

In the chemical characters and relations of metals and of metalloïds, there are differences as great as in their physical characters. These differences, however, are manifested more in the functions which the substances of one or other class perform, in their compounds with other substances, than by the capability of direct combination with each other, which is considerably influenced by various physical conditions, such as temperature, state of aggregation, &c.; hence also this mode of chemical action should probably be regarded merely as a phase of some more general dynamic property, rather than as the exercise of a peculiar force, inherent in the different elementary substances. (See CHEMICAL AFFINITY, i. 850 *et seq.*) But in any case, the existence of chemical compounds, and their characters in relation to other substances, must be regarded as results of the same mutual activity which determines chemical combination. Probably all elementary substances are more or less capable of existing in a state of chemical combination with each other; but those possessing this capability in the highest degree are, as a rule, either the most opposite in their general chemical relations, or else capable of assuming special functions in relation to certain others. The elementary substances possessing the most universal capability of existing in combination with others, and of direct combination, are fluorine? oxygen, sulphur, chlorine, bromine, iodine, and some of the metals.

Hydrogen and oxygen, which present the most decided differences in their general chemical relations, may be taken as typical of the two classes of elementary substances —metals and metalloïds—the one representing the basylous, and the other the chlorous constituents of compounds. (Graham.)

The basylous or chlorous characters of the elementary substances are not however absolute, except perhaps in the case of fluorine and oxygen. On the contrary, they vary according to the kind of substances existing in combination. Thus, for instance, chlorine and sulphur are both basylous in relation to oxygen, but chlorous in relation to hydrogen and most other elementary substances; again, among the metals which are generally basylous in their relations to other substances, some are capable of existing in combination with others, in relation to which they are then feebly chlorous.

In compound substances consisting of two elementary radicles, their chemical characters and relations to each other generally approximate to the basylous or chlorous condition more or less in proportion to the relative preponderance of one or other of those characters in one of the constituents. Thus, for example, in water the relatively basylous and chlorous characters of hydrogen and oxygen are so nearly balanced that it is almost destitute of any chemical activity as an independent substance, and that which it does exhibit is, according to circumstances, sometimes basylous, as in hydric sulphate, nitrate, &c., and sometimes chlorous, as in potassium-hydrate, calcium-hydrate, &c.

In hydrochloric acid, however, the chlorous character of chlorine relatively to hydrogen exceeds that of oxygen, in such a degree that this substance is decidedly chlorous in relation to those substances with which it can exist in combination. But in hypochlorous acid, though chlorine is basylous relatively to oxygen, that substance is feebly chlorous in its compounds. In soda and sodium-chloride, on the contrary, the basylous character of sodium exceeds that of hydrogen, relatively to oxygen and chlorine, in such a degree that the former is highly basylous, and the latter slightly so.

The chemical activity of compounds as independent substances, is not by any means proportionate to that of their constituents; thus, for instance, nitrogen is one of the most indifferent substances, but its compound with hydrogen is a powerful alkali, and some of its compounds with oxygen are powerful acids.

The proportion in which two elementary substances are combined also influences the chemical characters and relations of the compound. Thus, in sodium-peroxide, containing twice as much oxygen as soda does in proportion to sodium, the basylous character disappears, and this compound is destitute of any chemical activity as an independent substance. Again, manganous oxide is highly basylous, and manganic oxide slightly so, while the peroxide is indifferent, and the higher oxides are chlorous. In like manner the compounds of nitrogen and of chlorine, bromine, iodine, &c. with oxygen, are more decidedly chlorous in proportion to the amount of oxygen they contain.

The chemical function of manganese in manganous oxide is essentially different from that which it exercises in manganic or permanganic acids. In the former case the metal corresponds with, and is chemically equivalent to, hydrogen in water; in the latter case it corresponds with, and is equivalent to, chlorine and nitrogen in chlorous and nitrous acids, and to chlorine in perchloric acid. (See Classification, i. 1007; and Equivalents, ii. 491.)

Certain compounds of elementary substances present, in their general chemical relations and functions, a very close analogy with the metals and metalloïds; as, for instance, cyanogen (see ii. 275) and the hydrocarbon radicles. (See Radicles.)

Compounds are usually named generically according to their chlorous constituents, and specifically according to their basylous constituents; thus compounds in which oxygen, sulphur, or chlorine, &c., are the chlorous constituents are termed *oxides*, *sulphides*, *chlorides*, &c. (see Nomenclature). In the case of compounds in which the relative basylous and chlorous functions of the constituents are less marked or not easily determinable, names of a more arbitrary nature are commonly used; thus, for instance, the compounds of metals with each other are termed *alloys*, and those alloys in which one of the constituents is mercury are termed *amalgams*.

Since the specific descriptions of particular compounds will be found under their respective heads, it does not come within the scope of the present article to do more than point out the leading characteristic features of the most important classes of compounds, viz. oxides, sulphides, &c.

Oxides. All the elementary substances, except fluorine, are capable of existing in combination with oxygen, in one or several proportions.

The physical characters of oxides are generally very different from those of their constituent basylous radicles. Among the metalloïdal oxides, some are gaseous under ordinary conditions, as carbonic oxide, carbonic acid,* some of the nitrogen oxides, sulphurous acid, &c.; some are liquid, as nitrous acid; others are solid, as nitric acid, sulphuric acid, silica, &c. Among the metallic oxides, all of which are solid, some are volatilisable, as arsenious acid, antimonious oxide; the others are fixed and mostly infusible and insoluble in water. Formerly metallic oxides were called calces, and their production was termed calcination. (See Gas, ii. 774.)

Many oxides occur native in great abundance; thus among those of the metalloïds, carbonic acid is a constituent of the atmosphere and of a great number of mineral substances. Silica also is very abundant both in the states of quartz, flint, sand, &c., and as a constituent of numerous minerals and rocks. Sulphuric acid occurs frequently as a constituent of various minerals, as gypsum, selenite, heavy spar, &c.: boracic acid occurs in the lagoons of Italy, and in some minerals: phosphoric acid is very widely distributed throughout the mineral kingdom, in small relative quantity, and it occurs abundantly in plants and animals. Among the metallic oxides, water, the earths, and the alkalis are probably the most abundant; existing as constituents of various minerals and rocks. Among the compounds of the heavy metals with oxygen, the oxides of iron, manganese, and zinc are the most abundant, either as such or in combination with carbonic acid, silica, &c.

The chemical relations of the oxides are as diverse as those of elementary substances. Among the metalloïdal oxides containing the smallest proportions of oxygen, some are characterised by their chemical indifference, as individual substances, in relation to most other substances, as for instance carbonic oxide, nitrous oxide, &c. Those containing larger proportions of oxygen are possessed of considerable chemical activity; and, in their compounds with other oxides, they present relations which are generally of a more or less decidedly chlorous character, as for instance sulphuric, nitric, and carbonic acids.

The metallic oxides containing the smallest proportions of oxygen are sometimes characterised by their chemical indifference, as for instance suboxide of lead; but they more generally present relations of a basylous nature in their compounds with other oxides, as for instance potash, soda, zinc-oxide, silver-oxide, &c. Among those containing larger proportions of oxygen, some, such as ferric oxide, alumina, &c., present this character in a less marked degree, and in some of their compounds they are chlorous, as in potash-aluminate, &c. Other metallic oxides containing still larger proportions of oxygen, such as manganese-peroxide, &c., are mostly indifferent as individual substances; but the oxides containing the largest proportions of oxygen are in many cases decidedly chlorous in their compounds with other oxides; as for instance, manganic acid, permanganic acid, stannic acid, chromic acid, &c.

The chemical relations of compounds consisting of two different oxides are generally of a nature corresponding to those of hydrochloric acid and potassium-chloride to other chlorides, and the mutual relations of their constituents correspond with those of hydrogen and chlorine in hydrochloric acid. (See Salts; and Acids, i. 39; Alkali, i. 115; Base, i. 519.)

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* The word "acid" in this article is used in the sense of *anhydrous acid* or *anhydride*, *e.g.*, carbonic acid CO^2; nitric acid N^2O^5, &c.

Many oxides containing the largest proportions of oxygen are decomposed at various temperatures by the action of heat alone, yielding oxygen-gas and lower oxides. Excepting nitric acid, which is readily decomposed by heat, most of the other higher oxides of the metalloïds which are known in a separate state, are capable of supporting high degrees of temperature without decomposition. The sesquioxides and peroxides of metals are generally decomposed by heat into oxygen and lower oxides, and all the oxides of silver, gold, platinum, &c., are decomposed by moderate degrees of heat into oxygen-gas and the respective metals. Some oxides, on the contrary, combine with a further quantity of oxygen, either at the ordinary temperature, as for instance manganous and ferrous oxides, or when heated in contact with oxygen or atmospheric air, as plumbous oxide. This change takes place most readily in some cases when the oxide is in combination with water, or when water is present.

Most oxides may be decomposed to a greater or less extent by the simultaneous action of heat and of some other substance capable of combining with oxygen, and of abstracting it from the oxide operated upon, so as to form an oxide of greater stability under the circumstances. This reduction, as it is termed, is complete when the whole of the oxygen is separated from the basylous radicle, and partial when there is only a lower oxide produced. The most powerful reducing agents are the alkali-metals, hydrogen, carbonic oxide, and carbon. Even carbonic oxide is decomposed by potassium or sodium with the aid of heat. The oxides of the metalloïds are mostly susceptible of reduction by carbon with the aid of heat. Among metallic oxides those of iron, copper, lead, bismuth, &c., are completely reduced by hydrogen at a red heat; the oxides of manganese and uranium, &c., are but partially reduced; oxide of zinc with difficulty; while the lower oxides of chromium, manganese and uranium, and the oxides of the earthy and alkali-metals are not affected by hydrogen. In the reduction of metallic oxides by means of carbonic oxide or carbon, the metal eliminated often contains carbon in a state of combination with it. At very high temperatures, carbon reduces some oxides which are not affected by hydrogen, as for instance soda and potash at a white heat.

When the reduction of a metallic oxide by carbon is effected at a comparatively low temperature, carbonic acid is formed; but when it takes place only at a very high temperature, carbonic oxide is produced.

The reduction of metallic oxides may also be effected by heating them with metals whose oxides are less readily reduced. Thus potassium reduces several metallic oxides, and among others ferric oxide at a red heat; but at a white heat, potash is decomposed by iron. The result in this latter case may be due to the volatility of potassium at that temperature, and the consequent removal of small portions reduced under the influence of a preponderating mass of iron, so that this action takes place repeatedly until the whole of the potash is decomposed, and without any possibility of action between the potassium and oxide of iron.

By the action of heat and reducing agents upon compound oxides, such as sulphates, phosphates, &c., there may be produced a compound of the metal with the chlorous radicle, as sodium-sulphide, by heating to redness a mixture of the corresponding sulphate with carbon. If the radicle of the chlorous constituent of the compound does not combine with the metal under the circumstances, it may be volatilised in the state of a lower oxide, as in the reduction of nitrates.

Some compound oxides, such as carbonates, nitrates, &c., are decomposed by the mere action of heat, the acid being eliminated either unaltered or decomposed, and the metallic oxide remaining either in the same state as it existed in the original compound or in a higher state of oxidation; thus ferrous carbonate yields by ignition, ferroso-ferric oxide and a mixture of carbonic oxide with carbonic acid.

Certain metals and metalloïds do not, under any known circumstances, combine directly with oxygen; for example, gold, platinum, nitrogen, chlorine, bromine, iodine, &c. All the others are capable of combining directly with oxygen, some of them a very low temperatures, as for instance sodium, potassium, &c.; others like copper, ir carbon, sulphur, phosphorus, &c., when heated to temperatures differing for each. all cases the direct combination with oxygen is attended with evolution of heat if it takes place rapidly, it is also attended with evolution of light. (See Combu i. 1089.)

The physical condition of substances capable of combining directly wit influences very much the facility with which the combination takes place. minute subdivision is most favourable, while a compact condition is most combination, especially when the resulting oxide is infusible at the produced by the combination, and forms a protecting crust over the substance. Thus pulverulent copper, heated to about 450° C., takes fi and is completely converted into oxide; but a plate of copper under the same conditions merely becomes covered with a crust of oxide. On the contrary, a red-hot iron wire continues to burn in oxygen gas, because the resulting oxide is melted at the temperature produced, and thus a fresh metallic surface is exposed to the action of the gas.

The indirect oxidation of metals and metalloïds may be effected by heating them with substances which evolve oxygen when heated, such as nitrates, chlorates, &c. Some metals, such as iron, zinc, &c., decompose water in the presence of acids, and form oxides which combine with the acid. Others decompose water alone at the ordinary temperature, like sodium, or by the aid of heat, like aluminium, magnesium, iron, &c. Others again decompose water in the presence of an alkali, and with the aid of heat, like aluminium and zinc. The behaviour of iron with water-vapour, and that of ferric oxide with hydrogen, present a striking illustration of the influence of circumstances on the exercise of chemical affinity. The production of ferric oxide in the one case, and the reduction of the same substance in the other, are most probably due to the respective preponderance of water-vapour relatively to hydrogen, and of hydrogen relatively to water-vapour, and also to the constant removal of the hydrogen and the water-vapour which are produced in the two cases by the action taking place. A similar influence is also manifested in the reduction of zinc-oxide by hydrogen. (Deville.)

The facility with which different metals combine with atmospheric oxygen under ordinary circumstances, varies very much. While the alkali-metals are rapidly oxidised even in dry air, neither gold, silver, nor platinum is at all affected in any case. Some metals, such as iron, however, which remain perfectly bright in dry air or even oxygen, rapidly become oxidised in moist air, and covered with a coating of oxide. The presence of acid vapours in the atmosphere facilitates this action upon most oxidable metals, but in the case of some it does not extend beyond the surface. Thus, for instance, zinc, when superficially oxidised by exposure to the atmosphere, does not undergo further oxidation, the portions underlying the crust of oxide being in fact protected by it. In the case of iron, on the contrary, the oxidation progresses until the whole of the metal is converted into oxide, or as it is termed rust, and it even proceeds with accelerated rapidity after the first oxidation of the surface has taken place: for the electropositive relation of the iron to oxygen is augmented by its contact with the ferric oxide, and its combination with oxygen is thereby facilitated so much that the metal is capable of decomposing water.

A different application of the same principle may be made the means of preventing the oxidation of iron. Thus if the metal is placed in contact with a substance which renders iron electronegative in relation to it, the affinity of iron for oxygen is reduced, and it becomes less liable to oxidation than it would otherwise have been. This fact has been practically applied in the galvanising of iron, which consists in coating iron with a thin layer of zinc which becomes electropositive in relation to iron, and though the zinc is thus rendered more liable to oxidation, it still protects the iron, since the oxidation of the zinc is only superficial, and the production of a thin film of oxide upon it prevents further action.

Sulphides. These form a very numerous class of substances, which, consistently with the chemical analogy between sulphur and oxygen, present in their general relations considerable similarity to the oxides. They contain various proportions of sulphur, and are accordingly termed *proto-*, *sesqui-*, *di-*, *tri-* and *penta-*sulphides. With the exception of carbon-disulphide, which corresponds to carbonic acid, the sulphides of the metalloïds are but little known: there appear to be several sulphides of phosphorus, and probably more than one sulphide of nitrogen. (Faraday, Quart. Journ. Sci. iv.; Soubeiran, Ann. Ch. Phys. [2] lxvii. lxxi.)

The sulphides are capable of forming compounds with each other—sulpho-salts—analogous to the compounds of oxides, in which the sulphides of the most basylous elementary radicles, and those containing the smallest proportions of sulphur—the sulpho-bases—are basylous in relation to sulphides containing larger proportions of sulphur and less basylous radicles—sulpho-acids. Thus potassium-sulphide combines with carbon-disulphide and with arsenic-pentasulphide, forming potassium-sulpho-carbonate and potassium-sulph-arsenate. The sulphides of the alkali-metals were formerly called liver of sulphur.

Many sulphides combine with water and some other oxides, as well as with chlorides and iodides, &c.

The physical characters of some metallic sulphides closely resemble those of the metals in certain particulars, such as the peculiar opacity, lustre, and density, especially when they are in a crystalline condition. They are generally crystallisable, brittle, and of a grey, pale yellow, or dark brown colour. The sulphides of the alkali-metals are soluble in water, most of the others are insoluble. They are more frequently fusible than the corresponding oxides, and some are volatilisable, as mercury-sulphide, arsenic-sulphide. Carbon-disulphide is an oily liquid, insoluble in water.

Metallic sulphides occur native in great abundance in the various forms of pyrites, blende, and glance. They are the principal sources from which certain metals, such as lead, copper, &c., are extracted.

Many sulphides, when heated out of contact with atmospheric air, do not undergo any decomposition; this is the case chiefly with those containing the smallest proportions of sulphur, such as the protosulphides of iron and zinc. Sulphides containing larger proportions of sulphur are partially decomposed by heat, losing part of their sulphur, and being converted into lower sulphides, or partially reduced, as in the case of iron disulphide. The sulphides of gold and platinum are completely reduced by heat.

Some sulphides may be decomposed by the simultaneous action of heat and of substances capable of combining with sulphur. Thus, for instance, silver, copper, bismuth, tin, and antimony sulphides are reduced by hydrogen; copper, lead, mercury, and antimony sulphides are reduced by heating with iron; but, in this case, some of the sulphide escapes decomposition, and combines with the iron-sulphide produced, forming a sulpho-salt.

Sulphides which are not reduced by heat alone, are always decomposed when heated in contact with oxygen or atmospheric air. Those of the alkali- and earth-metals are converted into sulphates by this means. Zinc, iron, manganese, copper, lead, and bismuth sulphides are converted into oxides, and sulphurous acid is produced; but when the temperature is not above dull redness, some sulphate is formed by direct oxidation. Mercury and silver sulphides are completely reduced to the metallic state. Some native sulphides gradually undergo alteration by mere exposure to the atmosphere, but it is then generally limited to the production of sulphates, unless the oxidation takes place so rapidly that the heat generated is sufficient to decompose the sulphate first produced. In the production of some metals for use in the arts, the separation of sulphur from the native minerals is effected chiefly by means of this action in the operations of roasting. (See METALLURGY.)

Some metallic sulphides are also decomposed by heating them in contact with water-vapour, with production of metallic oxides and sulphuretted hydrogen: lead, antimony, and mercury sulphides are but partially or little affected, and the sulphides of alkali- or earth-metals are converted into sulphates, hydrogen being eliminated.

Metallic sulphides are decomposed in like manner when heated with metallic oxides in suitable proportions, yielding sulphurous acid and the metal of both the sulphide and oxide. Metallic sulphates and nitrates exercise a similar action, yielding various proportions of metallic oxide and basic sulphates according to the proportions of the substances reacting.

Many metallic sulphides are decomposed by acids in the presence of water, sulphuretted hydrogen being evolved, while the metal enters into combination with the acid or the chlorous radicle of the acid. Nitric acid when concentrated decomposes most sulphides, with formation of metallic oxide, sulphuric acid, sulphur, and a lower oxide of nitrogen. Nitromuriatic acid acts still more energetically in a similar manner.

Most of the metals and metalloïds are capable of combining directly with sulphur when heated with it under suitable conditions. Gold and zinc do not combine directly with sulphur. The combination of metals with sulphur is attended with great evolution of heat, and also of light when it takes place rapidly, being in fact a true case of combustion in which sulphur takes the part of oxygen.

Sulphides are also produced by the action of metals upon sulphydric acid, both slowly at the ordinary temperature, and more rapidly by the aid of heat. Metallic oxides heated with excess of sulphur yield sulphurous acid and sulphides; sometimes a compound of sulphide and oxide, as in the case of manganese. The alkalis and earths do not yield sulphurous acid in this way, but hyposulphurous or sulphuric acid, which remains in combination with a portion of the base—liver of sulphur. Metallic sulphates heated with carbon are reduced, carbonic acid or carbonic oxide and sulphides being produced. Hydrogen gas exercises the same reducing action with production of water. Metallic oxides heated in contact with sulphuretted hydrogen or vapour of carbon-disulphide are converted into sulphides, with simultaneous production of water and carbonic acid or carbonic oxide according to circumstances.

Solutions of metallic compounds yield precipitates of metallic sulphides when mixed with solution of sulphydric acid, or of soluble sulphides. In the case of metals whose sulphides are decomposed by dilute acids, the sulphides are not precipitated unless there is an alkali added to neutralise the acid of the metallic salt.

Metallic sulphides are also produced by the reduction of sulphates by organic substances. Many native sulphides have no doubt been formed in this way.

Phosphides.—These compounds are but little known in a definite state; but they appear to be in general analogous to the sulphides in their chemical characters. The metallic phosphides are mostly brittle and fusible, and the presence of phosphorus in metals renders them hard and brittle. (See COPPER, ii. 73; IRON, iii. 327, 334, 399; LEAD, iii. 557.)

The phosphides of the alkali- and earth-metals are decomposed by contact with water, yielding oxides and phosphoretted hydrogen. Some of the phosphides are converted by ignition in contact with air into basic phosphates, part of the phosphorus being volatilised.

Metallic phosphides may be produced, either by heating the metals with phosphorus, by the reduction of phosphates with carbon or hydrogen gas, or by the action of phosphoretted hydrogen upon solutions of metallic compounds. Some metals cannot be combined with phosphorus by any of these methods.

Chlorides.—All the elementary radicles, excepting fluorine, are known to be capable of existing in combination with chlorine. The compounds of chlorine with the metals generally correspond to the oxides. (See METALLIC CHLORIDES, i. 894 *et seq.*)

Among the chlorides of the metalloïds, some correspond in their composition with the respective oxides, sulphides, &c. (See i. 899, 764, iii. 293.)

Bromides.—(See i. 672 *et seq.*)

Iodides.—(See iii. 284.)

Fluorides.—(See ii. 670 *et seq.*)

Nitrides.—With the exception of the nitride of carbon (see CYÀNOGEN, ii. 275), these compounds are but little known. The titanium-nitrides are among the most remarkable. Several other metals and metalloïds appear to form definite compounds with nitrogen in several proportions. (See CARBAZOTE, i. 757; BORON, NITRIDE OF, i. 635; COPPER, ii. 67; IRON, iii. 391; MAGNESIUM, iii. 754; also NITROGEN.)

Carbides.—Several metals appear to be capable of forming compounds with carbon, but their chemical history is little known. The most important are the iron-carbides (iii. 371 and 329; also COPPER, ii. 52). Manganese probably forms compounds with carbon analogous to the iron carbides.

Silicides.—The compounds of silicium with the metals are still less known than the carbides. (See IRON, iii. 334, and MANGANESE, iii. 816.)

Alloys.—Most metals are probably, to some extent, capable of existing in a state of combination with each other in definite proportions; but it is difficult to obtain these compounds in a separate condition, since they dissolve in all proportions in the melted metals, and do not generally differ so widely, in their melting or solidifying points, from the metals they may be mixed with, as to be separated by crystallisation in a definite condition. Exceptions to this are met with in the cooling of argentiferous lead (iii. 504 *et seq.*), the crystallisation of brass (see COPPER, ii. 48), and of gun metal (ii. 44).

Some metals cannot be made to mix or combine with each other when melted together, except in very unequal proportions. Thus lead retains only 1·6 per cent. zinc, and zinc only 1·2 per cent. lead (see Matthiessen and v. Bose, 1861, Proc. Roy. Soc.). Even when metals are miscible in all proportions, it is difficult to say whether there is actual chemical combination, as in the case of potassium and sodium, tin and antimony.

The chemical force capable of being exerted between different metals may, as a rule be expected to be very feeble, and the consequent state of combination would therefore be very easily disturbed by the influence of other forces. The stability of such metallic compounds is however greater in proportion to the general chemical dissimilarity of the metals they contain. But in all cases of combination between metals, the alteration of physical characters, which is the distinctive feature of chemical combination, does not take place to any great extent. The most unquestionable compounds of metals are still metallic in their general physical characters, and there is no such transmutation of the individuality of their constituents as takes place in the combination of a metal with oxygen, or sulphur, or chlorine, &c. The alteration of characters in alloys is generally limited to the colour, degree of hardness, tenacity, &c., and it is only when the constituent metals are capable of assuming opposite chemical relations, that these compounds are distinguished by great brittleness.

The formation of actual chemical compounds is indicated in some cases, when two metals are melted together, by several phenomena, viz. the evolution of heat, as in the case of platinum and tin, copper and zinc, &c. The density of alloys, also differs from that of mere mixtures of the metals. In the solidification of alloys the temperature does not always fall uniformly, but often remains stationary at particular degrees, which may be regarded as the solidifying points of the compounds then crystallising. Tin and lead melted together in any proportions always form a compound which solidifies at 187° C. The melting point of an alloy is often very different from the point of solidification, and it is generally lower than the mean melting point of the constituent metals.

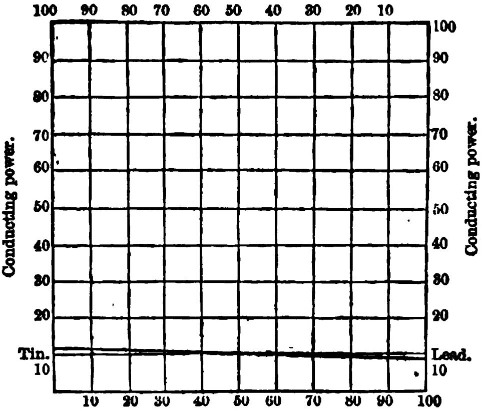
But though metals may combine when melted together, it is doubtful whether they remain combined after the solidification of the mass, and the wide differences between the melting and solidifying points of certain alloys appear to indicate that the existence of these compounds is limited to a certain range of temperature. Matthiessen (Brit. Ass. Reports, 1863, p. 37) regards it as probable that the condition of an alloy of two metals in the liquid state may be either that of—1. A solution of one metal in another; 2. Chemical combination; 3. Mechanical mixture; or, 4. A solution or mixture of two or all of the above; and that similar differences may obtain as to its condition in the solid state. He considers that the conductivity for heat and electricity are among the characters best calculated to indicate the chemical nature of alloys. In respect to electric conductivity, he divides metals into two classes, viz.:

A. Metals which, when alloyed with each other, conduct electricity in the ratios of their relative volumes—lead, tin, zinc, cadmium.

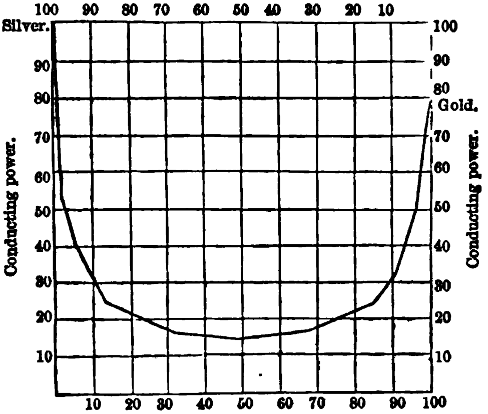
B. Metals which, when alloyed with each other, or with a metal of class A, do not conduct electricity in the ratios of their relative volumes, but always in a lower degree than that calculated from the mean of their volumes—bismuth, antimony, platinum, palladium, iron, aluminium, gold, copper, silver, &c.

The curves representing the conductivity of different series of alloys have the relation shown in the accompanying diagrams.

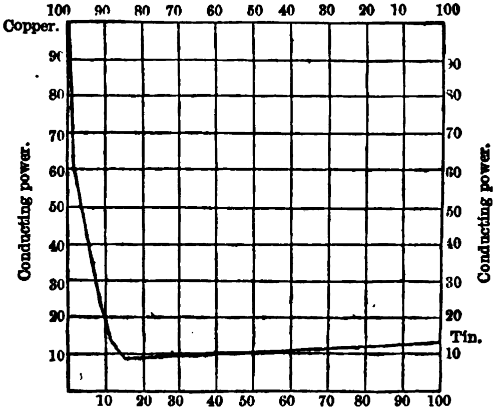
Group I.



Group II.



Group III.



Group I. Those belonging to the alloys of metals in class A are almost straight lines. That of the lead-tin alloys is given as the type.

Group II. The curves of alloys of metals in class B show a rapid decrement on both sides of the curve, the turning points being connected together by nearly straight lines. That of the gold-silver alloys is given as the type.

Group III. The curves of alloys of metals in class A with those in class B show a rapid decrement on the side beginning with the metal belonging to class B, then turning and going in a straight line to the other side, beginning with the metal belonging to class A. That of the tin-copper alloys is given as the type.

In regard to the alloys of the first group, if they were mechanical mixtures, the metals composing them, unless their specific gravities were the same, would separate into two layers when melted and slowly cooled, as in the case of the lead-zinc alloys (Matthiessen and v. Bose, Proc. Roy. xi. 430). But the alloys of lead and tin, for example, do not separate in the same way as lead and zinc. Moreover, homogeneous wires could not be obtained by pressing if these alloys were mechanical mixtures; but wires of the same alloy have been proved to have the same conducting power, whether taken from the press at the beginning or the end of the operation.

On the other hand, the agreement between the theoretic and actual conductivity of these alloys, as well as between the calculated and actual percentage decrement in conductivity between 0° and 100° C., indicates that, in the solid state, they are not chemical compounds. In regard to these particulars, the following law has been found to obtain for all alloys of the first and second groups, as well as for some of those belonging to the third group:

The actual percentage decrement in conductivity between 0° *and* 100° C. *is to the calculated decrement, as the actual is to the calculated conductivity.* (Matthiessen and Vogt, Proc. Roy. Soc. xii. 652.)

Among the alloys of the second group, some may be regarded as mechanical mixtures. Silver and copper fused and well stirred together, separate when slowly cooled, so that the mass contains different amounts of the metals at different parts (Levol, Journ. Pharm. xvii. 111). But these alloys are exceptional, and most of the alloys of this group may be regarded as solidified solutions of allotropic modifications of the metals in each other. The curves representing the conductivity of the different series of these alloys all have the typical form; and the decrement in conductivity between 0° and 100° C. agrees with the theoretical amount.

In the third group of alloys, the rapid decrement in the conductivity of those alloys of the several series which contain but very small amounts of a metal belonging to class A, cannot be ascribed to the existence of chemical compounds of the metals. For, in the first place, the amount of one of the metals in the alloys corresponding to the turning-points of the curves representing the conductivity of the series is too small, as will be seen by the following instances:

Alloy.	*Percentage.*
Bismuth-tin.	tin . . . 0·6
Bismuth-lead.	lead . . 2·0
Silver.	tin . . . 2·6

Again, the great similarity of the curves representing the conductivity of series of alloys belonging to this group, is opposed to the existence of chemical compounds in the solid alloys.

Moreover, the relation between the amount of different metals belonging to class A, and the decrement in conductivity of the alloys, is equally opposed to such a view of their condition. Thus in silver-lead and silver-tin alloys, the decrements in conductivity corresponding to 0·9 per cent. lead and 0·7 per cent. tin by volume are equal, and in bismuth-lead and bismuth-tin alloys, the decrements corresponding to 0·4 per cent. vol. lead and 0·62 per cent. vol. tin are equal. (See Matthiessen, Phil. Trans. 1860, p. 171.)

The influence exercised upon the conductivity of metals by the presence of small quantities of other metals does not appear to be in any way determined by the alteration of crystalline form or tendency to crystallise which are known to be influenced by that circumstance. (See Matthiessen and Vogt, Phil. Mag. 1862.)

If it be assumed that the metals belonging to class B undergo a molecular change when alloyed with one another or with metals belonging to class A, and that in each an allotropic condition is induced by a small amount of other metals, varying according to the different metals, then many of the phenomena characteristic of alloys may be explained. Thus, for instance, the curve representing the conductivity of zinc-copper alloys has the same form as those of other alloys belonging to the same group, and the percentage decrement in their conductivity between 0° and 100° C. is exactly what is indicated by the law above stated. Hence it may be inferred that solid alloys of zinc and copper are only solidified solutions of zinc and of allotropic copper in each other. The different action of reagents upon alloys and upon the metals constituting them, when in an isolated state, may also be referred to the existence of such allotropic modifications when they are alloyed, as well as to the existence of chemical compounds of the metals in the alloys.

In the tin-gold series of alloys, the curve representing the conductivity has not the typical form of this group of alloys. Beginning from tin there is a gradual decrement as far as the alloy Sn^5Au^2,* then a gradual increment to the alloy SnAu, and then a decrement to $SnAu^4$; and from the alloy containing 2·7 per cent. tin to pure gold, the increase of conductivity is represented by a straight line. These irregularities may be regarded as indicating that the alloys corresponding to the turning-points of the curve are chemical compounds, for they have definite composition; they contain large amounts of both metals: Sn^5Au^2 = 60 per cent.; SnAu = 37 per cent.; and $SnAu^4$ = 13 per cent. of tin. Then the specific gravity of the alloy Sn^5Au is almost equal to that calculated, while SnAu expands and $SnAu^2$ contracts more than any of the other tin-gold alloys. Moreover, the percentage decrement in the conductivity of these alloys between 0° and 100° C. does not conform to the law above stated (p. 943). Tin and gold also dissolve in each other very readily, with evolution of heat.

Matthiessen thus classifies the solid alloys composed of two metals according to their chemical nature.

1. Solidified solutions of one metal in another—lead-tin, cadmium-tin, zinc-tin, lead-cadmium, and zinc-cadmium alloys.
2. Solidified solutions of one metal in the allotropic modification of another—lead-bismuth, tin-bismuth, tin-copper, zinc-copper, lead-silver, and tin-silver alloys.
3. Solidified solutions of allotropic modifications of the metals in each other—bismuth-gold, bismuth-silver, palladium-silver, platinum-silver, gold-copper, and gold-silver alloys.
4. Chemical compounds of the alloys corresponding to Sn^5Au, Sn^2Au and Au^2Sn.
5. Solidified solutions of chemical compounds in each other—the alloys intermediate between those corresponding to the above formulæ.
6. Mechanical mixtures of solidified solutions of one metal in another—alloys of lead and zinc containing more than 1·2 per cent. lead or 1·6 per cent. zinc.
7. Mechanical mixtures of solidified solutions of one metal in the allotropic modification of another—alloys of zinc and bismuth containing more than 14 per cent. zinc or more than 24 per cent. bismuth.
8. Mechanical mixtures of solidified solutions of allotropic modifications of the two metals in each other—most of the silver-copper alloys. (Matthiessen, Brit. Ass. 1863—*Report on the Chemical Nature of Alloys*, pp. 37–48.)

In accordance with the rule generally obtaining in respect to chemical combination, the metals which present the greatest difference in their general chemical characters are the most capable of existing in combination with each other, and of forming definite compounds. Thus arsenic, antimony, &c., which are the most chlorous of the metals, form numerous definite compounds with the more basylous metals—silver, copper, iron, nickel, cobalt, &c., many of which compounds occur native. (See ARSENIDES and ANTIMONIDES, i. 316, 370, 591, 1041; ii. 41; iii. 368, 532.)

Some arsenides lose arsenic when heated out of contact with air; but by heating in contact with air they are converted into oxides or basic arsenates, while arsenious acid is volatilised.

These compounds are often formed in metallurgical operations with arsenical minerals containing cobalt, nickel, or iron, and collect in a separate layer between the reduced metal and the sulphides.

The physical characters of alloys, though they always retain the prominent characters of metals, are in some respects very different from those of the metals they contain, and which render these latter useful in the arts. Thus the alloy consisting of copper with half its weight of zinc, is much harder than pure copper, and at the same time sufficiently ductile (see BRASS, ii. 47 *et seq.*). The alloy of copper with one-ninth its weight of tin is much harder than copper, is well calculated for casting, and has sufficient tenacity for the construction of ordnance (see BRONZE, ii. 43 *et seq.*). The alloy of copper with one-ninth its weight of aluminium is hard, tenacious, and malleable (see ALUMINIUM BRONZE, i. 155). The alloy of copper with one-fourth its weight of tin is very hard, and being highly sonorous is well suited for bells, &c. The alloy of copper with half its weight of tin is white, and capable of receiving such a high polish as to be suitable for the reflectors of telescopes. (See SPECULUM METAL, ii. 43.)

The alloy of lead with one-fourth its weight of antimony is readily fusible, much harder than lead, but not brittle like antimony-bismuth or zinc, and is well suited by these characters for type-founding (see TYPE-METAL, i. 316; iii. p. 532). Other alloys will be found described under the heads of the several metals they contain.

The chemical action of reagents upon alloys is sometimes very different from their action upon metals in the separate state; thus platinum, when alloyed with silver, is readily dissolved by nitric acid, but is not affected by that acid when unalloyed. On the contrary, silver, which in a separate state is readily dissolved by nitric acid, is not dissolved by it when alloyed with gold in proportions much less than one-fourth of the alloy by weight.

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* S = 118; Au = 196.

Analysis of Alloys.—The number of metals which enter into the composition of the various alloys used in the arts is not very considerable, and in most ordinary cases the following systematic mode of testing alloys will serve to afford indications of what metals they contain.

The finely divided substance is covered with strong nitric acid in a glass flask, and the reaction is assisted by the application of a gentle heat.

I. *No reaction takes place*, and

A. The substance remains unaltered, indicating the probable absence of all metals but **gold** and **platinum.**

II. *A reaction takes place, red nitrous fumes being evolved;* and in this case:

B. Solution of the substance takes place without any residue being left, indicating the absence of **gold (platinum?), antimony** and **tin.**

1. The solution may contain all the other metals likely to be present in alloys, &c.; **copper, lead, silver, bismuth, mercury, arsenic, zinc, nickel, cobalt, iron, aluminium.**

C. The solution is partial, and the residue is—

2. *Metallic*, or a *black powder*, indicating the presence of **gold, platinum,** and perhaps **antimony** and **tin** in small proportions.

3. *White*, indicating the presence of **antimony** or **tin,** and perhaps **gold** and **platinum** in small proportions.

D. No solution takes place, indicating the absence of all metals but **gold, platinum, antimony, tin,** and perhaps **silver** and **lead** in small proportions. The residue may be—

4. *White*, indicating the same as 3.

The solution, 1, is in all cases to be treated in the same manner. When a residue remains undissolved, it is to be separated by decanting off the clear liquid, or by filtration after the excess of acid has been removed by boiling the liquid. The metals are then to be tested for in the clear solution. See Analysis, i. 216.

When, on treatment with nitric acid, there is produced an insoluble residue, 3, it is to be collected upon a filter, washed, and tested for tin antimony, &c. (See i. 322.)

When the substance is not acted upon by nitric acid, and when it is but partially dissolved, the residue, 2, or the unaltered substance, is to be treated with a mixture of three parts hydrochloric acid and one part nitric acid.

The result of this treatment may be either—

5. *Partial solution* and the separation of a white insoluble powder, chloride of **silver,** or (less probable) chloride of **lead.**

6. *Complete solution.* Both in this and the previous case, the metals belonging to this group A will be dissolved, and the solution may contain **gold** and **platinum,** which should be tested for in the usual manner. (See Analysis, i. 215, and Gold, ii. 928.)

The chloride solution, 5 and 6, may also contain metals which are only partially dissolved by nitric acid when alloyed with gold or platinum. B. H. P.

METALLURGY. *Hüttenkunde. Métallurgie.*—The art of extracting metals from the various minerals found in the earth, and of converting them into forms suitable for the purposes of the arts, which constitutes metallurgy in its widest range, comprises a number of operations which are of a purely mechanical nature, and which do not come within the province of this work. But many of the most important operations of metallurgy involve processes which are essentially chemical, and it is to the consideration of the general principles upon which these operations depend, that attention will be directed in this article. Information on the mechanical sections of Metallurgy will be found in *Ure's Dictionary of Arts, Manufactures, and Mines;* articles Metallurgy, Mining, and Ores, Dressing of.

The metals which are largely used in the arts, viz.: Iron, zinc, copper, lead, tin, antimony, bismuth, nickel, mercury, silver, gold, platinum, are, with the exception of the last two, chiefly found in the state of chemical combination with other substances, constituting a variety of minerals, among which those containing a sufficiently considerable amount of the several metals to admit of their being profitably extracted, are called ores, when they occur in sufficient abundance for metallurgic purposes.

The production of the alkali- and earth-metals, which is now carried on more extensively than it was, is a branch of industry appertaining rather to the chemical manufactory than to metallurgy; this is also the case with regard to the production of the compounds of cobalt, chromium, and arsenic which are manufactured from the ores of these metals.

The metallic compounds which are most frequent as ores are:—

1. *Oxides.* Either simple, such as stannic oxide in tin-stone, ferric oxide in hæmatite, or compound oxides, such as ferroso-ferric oxide in magnetic iron ore, and some saline compounds, as carbonates, and, in small quantity, silicates, sulphates, &c.

2. *Sulphides.* Either simple, such as galena, blende, grey antimony; or compound sulphides, such as copper pyrites, zinkenite, miargyrite.

3. *Arsenides.* Generally in small quantity, and mixed with other ores.

These compounds rarely occur in a separate state, but are more or less mixed with other minerals in which they are imbedded, Gang (*Gangue; gangart*), constituting masses which are situated in more or less horizontal or vertical positions relatively to the rocks they are associated with, and are accordingly distinguished by the terms bed (*Lager; amas*), or lode (*Gang; filon*).

The admixtures generally met with in ores are either minerals containing other metals than that of the ore they are associated with, or they are minerals which do not contain any of the metals commonly used for technical purposes, as for instance quartz, some one of the numerous mineral silicates, felspar, hornblende, mica, &c.; carbonates, calc-spar, bitter spar, limestone, &c.; sulphates, heavy spar; fluorides, &c., and portions of the rocks adjoining the lode or bed. Sometimes these latter admixtures are useful in the operations by which the metals are extracted; sometimes they require to be separated mechanically by various preliminary operations. (See ORES, DRESSING OF: *Ure's Dictionary of Arts, Manufactures, and Mines*, iii. 312.)

When the ores of a metal contain admixtures in small proportion of other metalliferous minerals, the operations by which the metal is extracted are in some cases considerably modified, with the view of effecting a separation of the foreign metals; either on account of their value, as in the case of argentiferous lead and copper ores, or because of their prejudicial influence upon the qualities of the metal to be obtained from the ore. (See COPPER, ii. 32; LEAD, iii. 504 *et seq.*)

The physical characters of the metals which it is the object of metallurgical operations to obtain, render it necessary that in most cases they should be melted before being used for practical purposes, and the chemical nature of their ores is such as to require the influence of powerful chemical agencies to effect the separation of the metals from the substances they are combined with. For these reasons, the action of heat in augmenting the chemical activity of substances has been had recourse to in most of the metallurgic operations by which chemical changes are to be effected in the ores or other materials operated upon, and the extraction of metals from their ores has therefore been commonly termed smelting. But there are other methods by which many metals may be extracted, and by which certain of them are to some extent extracted from their ores without the aid of heat. According to these methods, the ores are first operated upon in such a manner as to convert the metal they contain into a compound soluble in water, and from the solution the metal is separated either by the action of another metal upon the solution, or by galvanic action (ELECTRO-METALLURGY, *Ure's Dictionary of Arts, Manufactures, and Mines*, ii. 88). The influence of electricity, however, is chiefly applied in the working of certain metals for particular purposes, as in electroplating, and has not yet been rendered available in the extraction of the ordinary metals from their ores. Among the other methods of extracting metals from their ores in the wet way, the precipitation of copper (ii. 36) and the extraction of silver from its ores by means of sodium-chloride, after the silver in the ores has been converted into chloride (see SILVER), as well as the working of platinum and gold ores by nitro-hydrochloric acid, are the only methods of this kind which are carried on to any extent.

In metallurgic operations, conducted, as is usually the case, in the dry way, or without the presence of water, and with the aid of a high temperature, there are two modes in which chemical alterations are brought about in the ore or other materials operated upon, viz. melting and roasting. In the one case the material is mixed with some substance which decomposes it, when one or other of them is rendered liquid by heat. Thus, for example, galena and metallic iron melted together yield metallic lead and iron-sulphide. When galena is melted with litharge or lead-sulphate in suitable proportions, there are produced metallic lead and sulphurous acid (see *ante*, p. 482). A similar reaction takes place when cupric sulphide and cupric oxide are melted together. (See COPPER, ii. 23 *et seq.*)

In the other operation, viz. roasting, the ore, or other material, is subjected to the joint action of heat and of a gaseous substance capable of producing a chemical alteration calculated to facilitate a subsequent operation. Thus, for instance, in copper smelting, the ores consisting of sulphides, are roasted in contact with atmospheric air so as to convert them to a great extent into oxides, and in the subsequent melting operation the cuprous oxide is again converted into sulphide by reaction with the iron-sulphide remaining unoxidised, and is thus separated from the ferric oxide produced in the roasting. In the smelting of lead also, the galena is first roasted in contact with atmospheric air, and is thus partially converted into oxide and sulphate, which, in the subsequent melting operation, react with the remaining sulphide as above indicated.

In some cases the operation of melting is conducted with the view of effecting oxidation, as in the separation of antimony from gold, or of lead from gold and silver in cupellation (see *ante*, p. 508 *et seq.*). Roasting also is sometimes conducted with the object of effecting reduction, as in the conversion of metallic sulphates and arsenates into sulphides and arsenides by means of carburetted gases. But, as a general rule, the chief ultimate effect produced by roasting is oxidation, or some corresponding change; while the ultimate effect produced by melting is most frequently reduction. These operations are in some way involved in the extraction of all metals from their ores; a description of the general conditions under which they are conducted, and the general features of the chemical processes which take place under those conditions, will therefore exhibit the chief chemical principles of metallurgy. More detailed information will be found under the heads of the respective metals.

ROASTING OF ORES AND METALLURGIC PRODUCTS.

Ores and intermediate products are roasted either in the state of coarse powder, or as large lumps, according to their nature. The degree of heat applied is not in any case sufficient to cause fusion, or aggregation of the mass, and sometimes it is necessary to keep the material operated upon stirred about, so as to expose fresh surfaces to the action of the gas by which chemical alteration is effected.

Roasting is conducted, sometimes in kilns, sometimes in reverberatory furnaces specially constructed for the purpose, and sometimes the materials are merely piled up in heaps with alternate layers of fuel, which are ignited and allowed to burn slowly until consumed.

Oxidising roasting is always effected by means of a current of heated atmospheric air made to pass over the material at a suitable temperature. The chemical change produced by roasting is either a mere combination with oxygen, as in roasting magnetic iron ore, which is thus converted into ferric oxide; or it may be attended with the separation, more or less complete, of some constituent of the material operated upon, as in roasting sulphides, when a portion of the sulphur is converted into sulphurous acid and volatilised, while the metal is converted into oxide, and another portion of the sulphur is oxidised into sulphuric acid, which remains combined with the metallic oxide.

The different metallic sulphides present very different characters under these conditions: thus—

Iron-protosulphide is partially converted into ferrous sulphate: this at a higher degree of heat is decomposed into sulphurous acid, which is volatilised, and basic ferric sulphate, and ferrous oxide. At a still higher temperature the basic sulphate may be also decomposed, yielding at last ferric oxide. In operations on the large scale, however, it is very difficult to effect the entire separation of sulphur from iron-sulphide by roasting, even when the material is finely divided, the heat gradually applied, and the surface frequently changed by stirring meanwhile.

Zinc-sulphide undergoes oxidation very slowly, yielding a mixture of sulphate and oxide, which at a higher temperature loses sulphuric acid, and may be eventually converted into pure oxide. This result, however, is more difficult to obtain than in the case of iron-sulphide; but the roasting of zinc-sulphide is not so troublesome, inasmuch as it is less liable to undergo partial fusion than iron-sulphide is.

Copper-sulphide, when carefully roasted, is converted into a mixture of cuprous oxide and cupric sulphate. So long as sulphurous acid is being produced by the oxidation of sulphur, cupric oxide cannot be formed: for cupric oxide heated in contact with sulphurous acid is partially reduced, cuprous oxide and cupric sulphate being produced; but so soon as all the copper-sulphide has been converted into such a mixture, the cuprous oxide begins to be further oxidised. At a higher temperature, the cupric sulphate undergoes decomposition, sulphuric acid being more or less expelled. In the imperfect roasting of copper-sulphide, which is generally effected when ores containing that substance are operated upon on the large scale, the result is a mixture of cuprous oxide, cupric sulphate, copper-sulphide, and metallic copper. The latter appears to be produced in those places where the cuprous oxide is more highly heated, while surrounded by an atmosphere of sulphurous acid, than would be sufficient to reduce cupric oxide to cuprous oxide under the same condition.

Lead-sulphide is difficult to roast, since it is very liable to aggregate together, yielding a mixture of lead-sulphate and lead-oxide, from which the sulphuric acid cannot be expelled, even when it is heated so high as to melt.

Bismuth-sulphide is so fusible that it is very difficult to roast completely.

Antimony-trisulphide is also very difficult to roast for the same reason. There is generally produced a mixture of trioxide, pentoxide, and sulphide of antimony. If the heat be high, a portion of the pentoxide is volatilised.

Arsenic-sulphide and trisulphide are decomposed by roasting, yielding arsenious and sulphurous acids, both of which are volatilised.

Mercury-sulphide is converted by roasting into metallic mercury and sulphurous acid.

Gold-sulphide undergoes the same alteration by roasting.

Silver-sulphide is entirely converted into metallic silver. But when it is roasted together with other sulphides, such as iron- or copper-sulphide, some silver-sulphate is always produced, which by increase of temperature is decomposed into metallic silver, sulphurous acid, and oxygen.

Nickel-sulphide can be easily converted by roasting into a mixture of nickel-oxide and peroxide, with only a small admixture of unaltered sulphide. So long as sulphurous acid is generated abundantly, nickel-oxide only is produced, and this afterwards becomes peroxidised.

Cobalt-sulphide behaves in a similar manner to nickel-sulphide, except that some cobalt-sulphate is always produced.

In the roasting of sulphides, modifications of the chemical changes are often effected when reducing gases, such as carbonic oxide or hydrocarbons, are mixed with the atmospheric air; also, perhaps, when water vapour is present, as is almost always the case in this operation as conducted on the large scale.

The precise chemical alterations which arsenides and phosphides undergo when subjected to oxidising roasting, are less known than those of sulphides; but, as a general rule, arsenic is more difficult to separate than sulphur, and phosphorus can be separated only to a very small extent, on account of the stability of phosphoric acid at high temperatures.

Volatilising roasting. The sulphides containing the largest proportions of sulphur, such as iron-pyrites, &c., lose part of their sulphur by direct decomposition, in consequence of the mere action of heat. Hydrated compounds, carbonates, &c., are also decomposed in the same manner. But more generally the volatilisation of some constituent of the material roasted, is the result of previous chemical alteration, and its conversion into a volatile compound by the chemical action of the atmosphere in which the operation is conducted.

Chloridising roasting is effected by means of an atmosphere containing chlorine, hydrochloric acid, or chlorides. Silver ores are often subjected to this treatment, to convert the silver into chloride. At the same time, iron is partially volatilised as ferric chloride; arsenic, antimony, zinc, tin, bismuth, mercury, chromium and sulphur are also volatilised as chlorides.

Reducing roasting. When iron ores are heated in an atmosphere of reducing gases, such as carbonic oxide or hydrocarbons, metallic iron is produced; and in iron smelting this change always precedes the actual melting. When such ores contain zinc as well as iron, both metals are reduced, and the zinc is volatilised at a sufficiently high temperature. Under similar conditions arsenates and arsenites yield a portion of their arsenic in the metallic state. This is also the case with antimonates, tellurates, selenates, or sulphates.

MELTING OF METALLURGICAL PRODUCTS FOR THE EXTRACTION AND SEPARATION OF METALS.

Ores are rarely subjected to the operation of melting without having previously undergone some other treatment, such as roasting, &c. This preliminary treatment is in some cases only the earliest stage of the melting operation, as in the smelting of iron ores, which, in the upper parts of the blast-furnace, are subjected to the action of heat and reducing gases before sinking down to that part of the furnace where fusion takes place. (See IRON, *ante*, pp. 357, 364.) But in such cases, the chemical nature of the processes involved in the roasting and the melting is exactly the same as when these operations are conducted separately.

The chemical alterations which take place in the operation of melting sometimes result in the separation of a metal in the state of regulus, sometimes only in the partial separation of the substances combined with it, and the production of a matt (*Stein; matte*), or compound containing a larger proportion of metal than the material operated upon. (See COPPER, ii. 23 *et seq.*) These results are often due solely to the mutual action of the several constituents of the ore, which has undergone a preparatory treatment of roasting, &c.; but in most cases it is necessary to add some substance by means of which the desired result may be produced. The kind of substance to be added will of course be determined by the nature of the material to be operated upon, and by the kind of chemical alteration to be effected. Thus in smelting antimony ore, consisting of the trisulphide, it is mixed with scraps of metallic iron, by reacting with which it yields metallic antimony and iron-sulphide.

In all cases it is essential that in the melting operation there should be not only a chemical alteration of the materials, but also a physical separation of the resulting products. It is not often that this can be effected by the volatilisation of some one or more of the products. More frequently they are all fixed, and in this case they can be obtained separate only when they differ in specific gravity, and are also incapable of mixing with each other while in the liquid state. It is therefore always necessary, that in melting operations the whole of the materials should be rendered so liquid that such a separation may readily take place. The high specific gravity of the metals which it is the object of the metallurgist to obtain, is favourable to their separation as regulus, from the other products of the melting operation. The sulphides of these metals are also sufficiently dense to separate readily in the state of matt from most of the other products of melting, though their specific gravity is less than that of the metals.

With the object of facilitating the separation of the several products of the chemical action which takes place in melting operations, the ore or other material is generally mixed with some substance which has the capability of facilitating the liquefaction of the products formed, and their separation into distinct layers. Such an admixture added with the object of rendering some part of the material operated upon capable of being melted, or more readily fusible than it would be otherwise, is termed a flux (*Zuschlag; fondant*).

In the first melting of ores consisting chiefly of metallic sulphides, the product obtained is not always the metal, even when the ore has been previously roasted. More frequently a matt or mixture of sulphides is obtained, and if any metal is reduced to the state of regulus, the matt forms a separate layer above it. In melting ores containing much antimony, arsenic, &c., together with other metals, a third layer is sometimes formed, which separates between the regulus and the matt, and is called *Speise*.

But ores very generally contain, besides the actual metalliferous portion, a variety of siliceous or earthy admixtures, originating from the rocks and minerals with which they are naturally associated. These admixtures cannot be entirely separated by mechanical means, and since they are generally infusible or difficult to melt, they require to be converted into compounds which are sufficiently fusible, and of less specific gravity when melted, than the other products to be obtained. The fluxes added with this object are generally either—

Siliceous, such as quartz, sandstone, &c., or

Earthy, such as lime, limestone, clay, &c., according to the nature of the substances to be separated; by this means a fusible vitreous compound consisting of earthy silicates is formed, which is termed slag. Sometimes special fluxes are used, such as fluor-spar, alkaline salts, &c. (see p. 952).

The addition of fluxes in the melting operation is also advantageous in facilitating the fusion of the material operated upon, and the separation of the several products formed. Moreover, the resulting slag, being of less specific gravity than the other products, collects above them, and thus furnishes a protection against the oxidising action of the furnace gases, which is often a further advantage.

The melting operation is generally conducted either in shaft furnaces, where the materials are mixed with the fuel, or in reverberatory furnaces, where they are heated in a separate chamber by means of the flame and gaseous products of combustion. Sometimes crucibles are used in order to keep the materials entirely out of contact with the fuel.

Reducing melting is generally effected, in the case of metallic oxides, by the joint action of heat and the carbon, carbonic oxide, hydrocarbons or hydrogen contained in or resulting from the combustion of the fuel used in the operation. By reason of the unequal degrees of chemical stability of the several metallic oxides, the temperatures at which they are reduced by those substances differ considerably. The oxides of lead, bismuth, antimony, nickel, cobalt and copper are reduced by carbon within the range of red heat; while those of iron, manganese, chromium, tin, and zinc require more or less intense degrees of white heat.

The mode in which reducing melting is conducted varies according as the oxide is easily fusible or infusible at any temperature that can be attained in the operation. In the first case the material can be intimately mixed with carbon; in the second case this cannot be effected, and the reduction is to a great extent due to the carbonic oxide resulting from the combustion of carbon with a scanty proportion of air. (See IRON, p. 358.)

The reduction of metallic sulphides by melting is effected principally by means of metallic iron. Lead-sulphide melted with iron in equivalent proportions yields metallic lead, and iron-sulphide. With two equivalents of iron, there are produced metallic lead and iron-sulphide containing metallic iron mechanically mixed. Zinc-sulphide is completely decomposed by iron, but a very high temperature is required. Cuprous sulphide is partly decomposed by melting it with metallic iron, and there are produced a matt consisting of cuprous sulphide and iron-sulphide, and some metallic copper. The sulphides of copper and iron yield, on the contrary, a matt consisting of cuprous sulphide, iron-sulphide and metallic iron. Lead-sulphide with two equivalents of copper yields a matt consisting of cuprous sulphide and metallic lead. Equal equivalents yield metallic lead and a matt consisting of cuprous sulphide and lead-sulphide. Similar reactions take place between zinc-sulphide and copper.

Lead-sulphide is entirely decomposed by melting with an excess of tin, but in equal equivalents it is only partly decomposed, and there are produced an alloy of tin and lead and a matt consisting of tin-sulphide and lead-sulphide.

The metals of the alkalis exercise a much more energetic action upon metallic sulphides when melted with them, and though they cannot be employed in ordinary metallurgical operations, a similar action may be produced to some extent by means of a mixture of the alkalis and carbon (black flux). Thus, when a metallic sulphide is melted with a sufficient quantity of alkaline earth or alkali mixed with carbon, the metal is reduced, since the sulphur combines with the alkali- or earth-metal, while the oxygen of the latter combines with carbon. When an alkali is used, more or less of the metallic sulphide generally remains undecomposed and dissolved in or combined with the alkaline sulphide.

Oxidising melting is practised with the object of separating one metal from another, or of separating sulphur from metallic sulphides by converting the sulphur, or the metal to be removed, into oxides, which may either be volatile as sulphurous acid, fusible as oxide of lead, or capable of being rendered fusible by combination with certain substances added as fluxes.

Atmospheric air is the oxidising agent most commonly employed; but sometimes other substances are also used, which are capable of yielding oxygen at a high temperature, especially when in the liquid state and in contact with the substances to be oxidised. Among these are lead-oxide and oxy-salts, cupric sulphate, ferrous sulphate, basic ferrous silicate, nitrates, &c.

The following examples will serve to illustrate the mode in which these oxidising agents are employed in the melting operation.

Atmospheric air.—Compounds of gold or silver with antimony, arsenic, or sulphur, when melted in a sufficiently heated current of atmospheric air, are decomposed, and the metals are obtained in the pure state.

When atmospheric air is passed over the surface of melted copper containing iron, cobalt, lead, antimony, arsenic, and sulphur, the three latter are volatilised as oxides, and a more or less liquid layer or scum collects upon the surface of the metal, consisting of ferric oxide, cobalt- and lead-oxides, antimonic oxide, and cuprous oxide, until the copper remains almost pure. The greater the quantity of lead in proportion to the other impurities, the more liquid is the layer which collects on the surface; and the smaller it is, the thicker is this scum. In both cases the scum must be removed from time to time, so that a fresh metallic surface may be exposed, and if it is not sufficiently liquid to be removed by the current of air, the edges of the convex surface of melted metal where it principally collects must be raked off.

When alloys of gold or silver with lead or bismuth are exposed in a melted state to a current of air, the latter metals are oxidised, and pure gold or silver remains, together with a slag of lead-oxide. A portion of the oxide is volatilised, and in the case of silver-alloys especially, a small quantity of this metal is also volatilised. When small quantities of other metals, such as iron, cobalt, copper, &c., are present in such alloys, they are oxidised, and the oxides are dissolved by the oxide of lead or bismuth.

When a compound of arsenic, iron, cobalt, and nickel is melted in a current of air, so that the ferric oxide and cobalt-oxide produced may be dissolved by melted borax, partly covering the surface of the melted metal, arseniferous nickel may be obtained; but the whole of the arsenic cannot be separated, because, in proportion as it is separated, the melting point of the remaining metal becomes higher, and it finally solidifies.

Lead-oxide.—When litharge is melted with easily oxidisable metals, they are oxidised by the decomposition of the lead-oxide, a part of the lead-oxide is reduced, and a slag consisting of lead-oxide and the oxide of the metal is produced; but the perfect oxidation of metals possessing little affinity for oxygen cannot be effected in this way, without using a large excess of litharge.

Metallic sulphides or arsenides melted with litharge, yield sulphurous and arsenious acid, which are volatilised, and alloys of the metals with lead.

Iron-sulphide melted with thirty parts by weight of litharge is entirely oxidised, sulphurous acid being volatilised, while the iron remains probably in the state of ferroso-ferric oxide combined with the excess of lead-oxide, forming a slag which collects over the reduced lead. With less lead-oxide the decomposition is incomplete, and a part of the iron-sulphide passes into the slag.

The oxidation of cuprous sulphide in this way requires 25 pts. by weight of litharge.

The oxidation of copper pyrites requires at least 30 pts. of litharge. When less is used, the copper-sulphide remaining undecomposed is not dissolved by the slag consisting of lead-oxide and cuprous oxide, but forms a **matt** with a portion of the metallic lead.

Antimony-trisulphide is entirely decomposed by melting with about twenty-five times its weight of litharge, yielding antimonic acid and sulphurous acid.

Tin-sulphide requires for perfect decomposition 30 pts. of litharge.

Zinc-sulphide requires 25 pts. of litharge.

Bismuth-sulphide when melted with litharge yields sulphurous acid and an alloy of bismuth and lead, but no bismuth-oxide.

Lead-sulphide is decomposed by melting it with about twice its weight of litharge, the whole of the lead being separated in the metallic state, while sulphurous acid is volatilised. When the lead-sulphide is in excess, it mixes with the metallic lead.

Arsenic-trisulphide melted with from 50 to 60 pts. of litharge is completely oxidised, yielding sulphurous acid and arsenious acid.

Other metallic oxides react with metallic sulphides in a similar manner to litharge, and, as a general rule, when a metallic sulphide is melted with a metallic oxide, the former is oxidised to a greater or less extent, and the relative quantity of the oxide produced depends upon, 1st, the relative quantity of oxide used, and 2nd, the relatively chlorous and basylous characters of the metals and of sulphur and oxygen.

Lead-carbonate acts in the same manner as lead-oxide upon metallic sulphides and oxides.

Lead-silicate also acts in the same manner, but a much larger quantity is required to produce the same effects as litharge. The slags produced in this case are double silicates containing both metals.

Lead-sulphate is a still more powerful oxidising agent than litharge, since the decomposition of its sulphuric acid yields an additional quantity of oxygen. When it is melted with lead-sulphide in due proportions, the products are only metallic lead and sulphurous acid.

Cupric sulphate heated with metallic sulphides generally exercises an oxidising action like lead-sulphate.

Copper-sulphide heated with cupric-sulphate is converted into copper, cuprous oxide, cupric oxide, basic cupric sulphate, &c., according to the proportions and temperatures. Silver-sulphide is also converted into sulphate in the same way; but metallic silver may be separated by the action of cuprous oxide.

Ferrous sulphate acts in a similar manner with metallic sulphides.

Nitrates are too costly to be generally used in metallurgical operations, though they are the most powerful oxidising agents in melting operations.

Basic ferrous silicate is one of the most important oxidising agents in metallurgical operations. For instance, when iron containing carbon, silicium, sulphur, and other readily oxidable substances, is strongly heated with a melted basic ferrous silicate, half of the ferrous oxide is decomposed, and the oxygen thus eliminated combines with the above-named impurities of the iron, forming carbonic oxide, silica, and sulphurous acid.

Solvent melting is practised chiefly with the object of separating certain parts of the materials operated upon in the extraction of metals. The substances used for this purpose are principally metallic oxides, silica, alkaline and earthy salts, silicates, metals, and sulphides.

Metallic Oxides.—Easily fusible oxides, such as lead-oxide, &c., melted with other less fusible oxides, at sufficiently high temperatures, dissolve the latter to a greater or less extent, sometimes forming saline compounds. Certain sulphides are also dissolved by lead-oxide and bismuth-oxide without decomposition, forming compounds termed oxysulphides. In metallurgical operations, it is only the solvent action of lead-oxide which is of special importance, and that chiefly in the purification of silver. (See p. 951.)

As a general rule, all oxides which are readily fusible, like bismuth or antimony oxides, may be mixed with lead-oxide in all proportions by fusion, but the less fusible oxides yield with lead-oxide difficultly fusible mixtures.

Tin-sesquioxide dissolves in four parts by weight of lead-oxide, forming a viscid liquid; with eight parts of lead-oxide it forms a very fusible mixture.

Zinc-oxide dissolves in seven parts of lead-oxide, forming an easily fusible mass.

Ferric oxide dissolves in four parts of lead-oxide, forming a viscid liquid.

Cuprous oxide with one and a half times its weight of lead-oxide forms a very liquid compound, and is probably soluble to a still greater extent.

Among the metallic sulphides, those of gold, silver, copper, &c., do not dissolve in melted lead-oxide (see above). All the other sulphides are more or less dissolved by it. Antimony trisulphide appears to be especially soluble in lead-oxide.

Metals.—Lead is the metal principally used as a solvent in certain melting operations. It has the property, when melted with argentiferous and auriferous sulphides in due proportion, and by sufficiently intimate mixture, of dissolving out the silver and gold. This effect is due to the decomposition of the gold and silver sulphides by lead at a high temperature, in such a manner that these metals are eliminated while lead-sulphide is formed, while, at the same time, there is scarcely any decomposition of iron-sulphide or copper-sulphide in the same way. The products of the melting are therefore argentiferous or auriferous lead containing lead-sulphide, and a matt consisting of copper-sulphide and iron-sulphide. Gold or silver may also be extracted from metallic copper by means of lead, but in a less direct manner. Both the gold or silver and the copper are dissolved by the melted lead; but in the solidification of this mixture, the greater part of the lead separates, and there is produced a mechanical mixture of lead containing gold or silver, and of an alloy consisting of lead with three times its weight of copper, containing much less silver. When this mechanical mixture is heated to the melting point of lead, this metal may be separated, together with the gold and silver, while the copper-lead alloy remains behind.

Metallic sulphides, such as iron-sulphide, &c., may be used in the same manner as metallic lead for extracting gold or silver from ores or metallurgic products. Thus when silver ores containing large admixtures of gang, in the melting of which alone the greater part of the silver would pass into the slag, are melted with iron-sulphides, the silver is dissolved as sulphide, and the gangue forms a slag containing but little silver.

Silica is rarely used alone as a solvent in the melting operation, silicates or earths being generally present, with which it forms compound silicates. Its action in such cases is therefore indirect, and depends more upon the nature of the silicate produced. (See p. 954.)

Earthy oxides, such as baryta, strontia, lime, magnesia, and alumina, respectively form with silica sparingly fusible or infusible compounds, according as the basylous character of the earth in relation to silica, is greater or less, and according to the proportions of earth and silica. The fusible baryta-silicates contain from 30 to 70 per cent. silica; the others are infusible. Strontia-silicates are much less fusible; that containing 55 per cent. silica forms a white opaque mass. Among the lime-silicates the limits of fusibility are between 25 per cent. and 47 per cent. of lime. Magnesia-silicates, and especially alumina-silicates, are infusible, and soften only at a full white heat.

Metallic oxides form compounds with silica which present similar differences in fusibility, according to the greater or less basylous character of the oxide in relation to silica and the proportions in which they are combined. Thus ferrous silicates with from 42 to 82 per cent. ferrous oxide, are easily fusible, while ferric silicates are infusible. Cuprous silicate is fusible only when it contains 70 per cent. cuprous oxide. Cupric silicates are probably infusible, but on account of their liability to undergo reduction, they cannot easily be produced. Zinc-silicates and tin-silicates are infusible. Lead-silicates containing from 54 to 88 per cent. of lead-oxide melt more or less easily. Bismuth-silicates are still more fusible. Antimony-silicates are sparingly fusible.

Alkaline carbonates dissolve most metallic oxides to some extent, the carbonic acid being also partly expelled at a red heat. With a sufficient excess of alkaline carbonate some of these compounds are easily fusible (Berthier). Ferrous oxide melted with 6 pts. of potassium-carbonate yields a greenish crystalline mass. Ferric oxide appears to be insoluble in melted alkaline carbonates. Tin-oxide fuses readily with 5 pts. by weight of potassium-carbonate; zinc-oxide is less soluble. Cuprous oxide and cupric oxide melt easily with 3 pts. of potassium-carbonate. Lead-oxide mixes in all proportions with melted alkaline carbonates.

Borax is a very efficient solvent in melting operations, but is too costly to be much used in metallurgy. Baryta, lime, magnesia, and alumina are dissolved in considerable proportions by melted borax, forming more or less fusible vitreous masses (Berthier). Silica and fire-clay melt together with borax at high temperatures. All the metallic oxides which are not reduced by heat alone, are dissolved to a greater or less extent by melted borax. Ferrous oxide or ferroso-ferric oxide, melted with an equal weight of borax, forms a compact crystalline mass. Manganous oxide is dissolved in very considerable amount by borax. Lead-oxide and borax melt together in all proportions.

Fluor-spar is important as a solvent in melting operations, on account of its capability of dissolving about half its weight of silica at a high temperature, without having any tendency to combine with or dissolve metallic oxides. Fluor-spar is, therefore, a very suitable flux in the smelting of ores which are refractory on account of the silica they contain. Fluor-spar also dissolves sulphates which are infusible or difficult to fuse alone, such as heavy spar, gypsum, &c. Thus with 1⅓ pt. barium-sulphate, 4 pts. anhydrous calcium-sulphate, or 10 to 15 pts. lead-sulphate, fluor-spar forms vitreous masses which are tolerably fusible.

Silicates.—The earthy and alkaline silicates in a melted state have the capability of dissolving metallic oxides in considerable proportions, forming when cooled the vitreous or stony masses generally called slags. In metallurgic operations it is of importance that there should be a proper proportion between the silica and earthy bases in the materials from which the slag is produced in melting, in order that its solvent action upon the metallic oxides present may be neither too great nor too little. The former might be the case if there were too much silica; the latter if there were too little. Siliceous slags are generally of such composition that the ratio of the oxygen in the bases to that in the silica is approximatively either as 1 : 3, 1 : 2, or 1 : 1. From the nature of the silicates generally and from the circumstances under which slags are produced in metallurgical operations, it is of course rarely that they are definite chemical compounds. Slags may indeed contain definite compounds, but in almost all cases they are merely heterogeneous mixtures of such compounds with other adventitious substances, and therefore the attempt to represent their composition by formulæ is not only useless but deceptive. The utmost that can at present be said with regard to the composition of slags is, that there are certain tolerably constant relations between the fusibility, &c. of slags and the ratio of the oxygen in the bases to that in the silica. The numerous analyses of slags from different metallurgic operations all afford evidence in favour of this view, and from among them the following selections will serve to represent the general composition and limits of variation in slags.

	Blast furnace slags, from iron smelting.				Slags from copper smelting.			Lead slag.
Names of Works.	Creusot.		Gesberg.		Röraas.	Nafvequare	Freiberg.	Sala.
Analyst.	Guenyveau.		Ongren.	Sjögren.	Johnson.	Bredberg.	Winckler.	Bredberg.
Silica . . .	39·5	49·6	58·6	61·1	31·4	56·5	51·4	39·4
Alumina . .	18·0	15·0	6·6	5·4	7·9	9·4	4·8	6·2
Ferric oxide .	3·0							
Manganous oxide	trace	. .	2·8	2·6				
Ferrous oxide .	. .	3·0	1·7	3·3	55·2	6·2	34·1	17·2
Lime . . .	35·6	30·0	9·3	19·8	. .	20·0	. .	17·8
Magnesia . .	. .	. .	10·5	7·1	4·5	6·4	7·6	19·1
	96·1	97·6	89·5	99·3	99·0	98·5	97·9	99·7
Ratio of oxygen in bases to oxygen in silica	1 : 1	1 : 1·5		1 : 2·5	1 : 1	1 : 2·5	1 : 2·5	1 : 2

The solvent action of earthy silicates upon metallic oxides is especially serviceable in effecting the separation of the ferrous oxide, produced by the oxidising roasting of ores and certain products of metallurgic operations, such as copper-matts, &c. Thus when a mixture of ferric oxide, cuprous oxide, and a silicate containing excess of silica is subjected to reducing melting, the cuprous oxide and the ferric oxide are both reduced, the former yielding metallic copper, and the latter ferrous oxide, which combine with the silicate, forming a fusible slag which admits of the metallic copper separating out and collecting together in mass below it. Manganic oxide, or cobalt-oxide, &c., would behave in the same manner as ferric oxide; and any easily reducible oxide, in the same manner as cuprous oxide.

Silicates also exercise a solvent action upon the gangue mixed with ores. Thus for example, when an ore consisting of galena and gangue is melted, with addition of ferric oxide and suitable slags, the latter dissolve the gangue, the ferric oxide is reduced to ferrous oxide, which reacts with the lead-sulphide, and oxidises a portion of the sulphur to sulphurous acid, which volatilises, while the metallic iron produced at the same time, separates the lead from combination with the remaining sulphur, and forms iron-sulphide. In this case all the different reactions produced in melting operations take place together.

As a general rule it may be stated, that when mixtures of an oxide with another oxide which is more easily reduced, and of silicates containing a sufficient amount of silica, are subjected to reducing melting, the least easily reducible oxide is dissolved by the silicate and forms slag, while the more easily reducible oxide yields metal. To obtain this result, however, it is necessary that the silicate should be present in sufficient amount, and that its melting point should be higher than the temperature at which the more easily reducible oxide is decomposed, and lower than that at which the less easily reducible oxide is decomposed. If there were a deficiency of silicate, the whole of the ferrous oxide would not be converted into slag, and a portion of it would be reduced to the metallic state. If the silicate melted before the cuprous oxide had been reduced, part of the latter would pass into the slag; and if it did not melt till after ferrous oxide had been partly reduced, the copper would be mixed with iron.

Slags should in general be more easily fusible, or at most not less fusible than the other products of the melting operation; but the actual degree of fusibility will vary considerably, according to the temperature requisite in the operation. The following table contains a summary of the more important results obtained by Plattner in his investigation of the fusibility of various silicates and slags:—

Temperature of formation.	Melting point.	Silica.	Baryta.	Lime.	Magnesia.	Alumina.	Ferrous oxide.	Manganous oxide	Lead xide	Ratio of oxygen in bases to oxygen in silica.
2200° C.	. .	29·1	70·9	. .	. .	. .	. .	. .	. .	1 : 2·1
2100°	. .	37·6	62·4	. .	. .	. .	. .	. .	. .	1 : 3
2150°	. .	52·0	. .	48·0	. .	. .	. .	. .	. .	1 : 2
2100°	. .	61·8	. .	38·2	. .	. .	. .	. .	. .	1 : 3
2250°	. .	59·8	. .	. .	40·2	. .	. .	. .	. .	1 : 2
2200°	. .	69·0	. .	. .	31·0	. .	. .	. .	. .	1 : 2·8
2400°	. .	64·3	. .	. .	. .	35·7	. .	. .	. .	1 : 2
2400°	. .	73·0	. .	. .	. .	27·0	. .	. .	. .	1 : 3·2
2100°	. .	48·6	10·0	41·4	. .	. .	. .	. .	. .	1 : 2
2100°	. .	45·0	20·0	35·0	. .	. .	. .	. .	. .	1 : 2
2050°	. .	54·0	20·0	. .	. .	26·0	. .	. .	. .	1 : 2
2000°	. .	55·5	. .	25·8	18·7	. .	. .	. .	. .	1 : 2
1918°	. .	40·5	. .	37·2	. .	22·3	. .	. .	. .	1 : 1
1950°	. .	57·5	. .	26·5	. .	16·0	. .	. .	. .	1 : 2
1789°	. .	30·5	. .	. .	. .	. .	69·5	. .	. .	1 : 1
1832°	. .	47·0	. .	. .	. .	. .	53·0	. .	. .	1 : 2
Iron blast furnace slags.										
1876°	1431°	50·0	. .	30·0	. .	17·0	3·0	. .	. .	1 : 1·5
Freiberg copper slag. 1445°	1445°	58·0	. .	22·0	10·0	6·0	2·0	2·0	. .	1 : 2·2
1690°	1331°	48·0	. .	4·5	1·5	9·0	37·0	. .	. .	1 : 1·75
1730°	1360°	50·0	1·5	3·0	1·5	6·0	38·0	. .	. .	1 : 2
Freiberg lead slag.										
1460°	1317°	36·5	. .	4·0	3·0	8·5	40·5	. .	7·5	1 : 1·25
Freiberg copper slag.										
1546°	1345°	32·7	. .	. .	. .	7·0	60·3	. .	. .	1 : 1

The temperatures given as those at which these silicates were formed and melted refer to the melting points of platinum 2534° C., gold 1102° C., silver 1023° C., and lead 334° C., adopted by Plattner as the standards of comparison in his experiments.

The fluidity of slags differs very considerably, and it is often of great importance in practice. The mode in which they solidify also is of still greater importance. Some are very liquid, but change at once by reduction of temperature from the liquid to the solid state; others are less liquid, and solidify gradually, passing through several stages of viscidity.

The former always contain a smaller proportion of silica than the latter; and the characters of slags, while in the melted state, and after solidification, often furnish the practised metallurgist with indications as to whether the materials he is operating upon are duly proportioned or not.

Slags are sometimes amorphous, sometimes crystalline. The former are often glassy; the latter present an appearance resembling certain rocks, such as lava, and in composition they often approximate to augite, olivin, felspar, &c.

SUBLIMATION AND DISTILLATION.

Volatilisable metals and metallic compounds are in some cases separated from their ores by means of that character. Thus arsenious acid, arsenic sulphide, and cinnabar are separated in this way from other substances with which they may be mixed or combined. The native compounds of iron with arsenic are decomposed by heat, yielding metallic arsenic, which is volatilised, while a lower arsenide remains. Arsenical pyrites heated in a close vessel yields arsenic sulphide at first, and finally metallic arsenic, about half the sulphur and rather less of the arsenic remaining combined with the iron. When mercury ores are heated with some substance capable of forming a fixed compound with any constituent of them which is capable of being volatilised in combination with the metal, metallic mercury distils off. Zinc-carbonate, intimately mixed with carbon and exposed to a white heat, is decomposed after losing its carbonic acid; the carbonic-oxide produced by the partial combustion of the carbon reduces the zinc-oxide, and the metal is volatilised.

ELIQUATION AND CRYSTALLISATION.

These operations are practised with the object of separating mixtures of substances which have different melting points, or which solidify at different temperatures. Argentiferous lead is separated from a mixture of lead and copper containing silver (see p. 953), by heating it in such a manner that when the lead melts, it can flow away from the alloy of copper and lead which remains solid. Silver is separated from argentiferous lead by crystallisation, since the alloy of lead with the largest proportion of silver does not solidify until the alloy of lead with the smallest proportion has separated in crystals. (See p. 504.)

The metallurgical operations already treated of being all conducted with the aid of heat, involve the use of fuel as a source of heat; and it is therefore an object of great importance to apply it to this purpose in the most efficient and economical manner. The general principle by which the relative value of different kinds of fuel may be determined, and the conditions under which they may be rendered most efficacious, have been already considered. (See FUEL, ii. 718 *et seq.*) It now only remains to refer simply to the means of augmenting the efficacy of fuel beyond its natural capability, so far as relates to the production of high temperatures by the application of heated air in the combustion of fuel. The advantage gained in this way always involves the consumption of a proportionately larger amount of fuel according to the degree of temperature produced; but since the metallurgic operations which require a very high temperature can be conducted much more rapidly in proportion as the temperature is increased, the saving of fuel effected by using a high temperature is referable to the larger quantity of material which can be worked within a given time, compared with what can be worked within the same time at a lower temperature.

Whenever it is necessary to use fuel in such a manner that only a portion of its heating power is rendered effective, as in most of the operations connected with the manufacture of iron, a very great economy can be effected by using the waste gases for the purpose of heating the air with which the furnaces are fed, instead of allowing those gases to escape without producing any useful effect. The heat thus communicated to the air with which the furnaces are fed has the effect of raising the temperature produced in those furnaces to a degree far higher than can be produced by the mere combustion of the fuel used. This augmentation of temperature is of course proportionate to the increased temperature at which air is supplied to the furnaces, and since the production of a very high temperature is the essential condition by which economy of fuel is to be attained in the manufacture of iron, the means of insuring this object are of the highest importance. (See IRON, iii. 362 *et seq.*, and FUEL, ii. 729.)

In many metallurgic operations, the use of gaseous fuel obtained by burning coal, &c., so as to convert it into carbonic oxide and hydrocarbon gases, is capable of being made a very valuable means of effecting economy in fuel, and at the same time of obtaining more advantageous results as regards the metals produced; but as yet little progress has been made in this direction compared with the capabilities which exist for such a use of fuel.

The use of air containing a larger amount of oxygen than atmospheric air would also be a very efficient means of economising fuel, especially in operations requiring high temperatures or intensity rather than quantity of heat. Some attempts have already been made to realise the advantages of such a practice, but they have not hitherto been attended with any such success in relation to the larger metallurgic operations as to require more than a passing mention. (See FUEL, ii. 725.)

The metallurgic operations which are conducted without the aid of a high temperature, and by the agency of water or other solvents, according to what is termed the wet way, are but few, viz. the extraction of platinum and silver, the separation of gold from silver, and to a less extent the extraction of copper from some of its ores.

SOLUTION AND PRECIPITATION.

By the first of these operations silver is extracted from its ores as sulphate, or by means of a solution of sodium-chloride, after the metal has been converted into chloride. Platinum is also extracted from its ores by means of nitro-hydrochloric acid, and silver is separated from gold by treatment with nitro-hydrochloric acid, which dissolves only the latter metal; or when the silver amounts to more than three times as much as the gold, by means of nitric acid (see GOLD, ii. 925), which dissolves only the silver, this operation being termed parting. Copper is also extracted from poor ores by converting it into chloride or sulphate, and dissolving these salts out with water. (See COPPER, ii. 36.)

Another operation involving solution is the extraction of gold and silver from their ores by means of mercury, which is frequently practised under the name of amalgamation, since the solution of the metals by mercury depends upon the formation of an amalgam, which dissolves in excess of mercury. (See GOLD, ii. 925, and SILVER.)

Precipitation is practised for the separation of metals from the solutions obtained from ores as above mentioned. Thus copper is precipitated in the metallic state by means of metallic iron, which decomposes the copper-compound held in solution. This operation is termed *cementation*. (See COPPER, ii. 36.) Platinum is separated from solution as ammonio-chloride, by precipitation with solution of sal-ammoniac; silver as chloride, by means of solution with salt, or hydrochloric acid; and gold, in the metallic state, by means of ferrous sulphate. (See GOLD, ii. 925.)

The various operations of metallurgy which are conducted by means of electrolysis, such as electroplating, electrogilding, and electrotyping, depend upon the principles which have already been discussed in general terms in the article ELECTRICITY (ii. 414 *et seq.*, and 437); and more precise details will be found in *Ure's Dictionary of Arts, Manufactures, and Mines*, article ELECTRO-METALLURGY.

The methods of manufacturing aluminium, magnesium and sodium, &c., will be found in the articles devoted to the general chemistry of those metals. B. H. P.

METALS, ATOMIC WEIGHTS AND CLASSIFICATION OF. GROUP I. Monad metals.—The received atomic weights of the non-metallic monads, fluorine, chlorine, bromine, and iodine, or 19, 35·5, 80, and 127, are merely the relative weights of each of them which have the same gaseous bulk as the unit of hydrogen. These four halogen elements, which may be considered as chlorous or electro-negative varieties of hydrogen, have the characteristic property of replacing hydrogen and one another, in a great variety of compounds, by an equivalent substitution of volume for volume, atom for atom. The fluoride, chloride, bromide, and iodide of hydrogen are composed of equal volumes of halogen and hydrogen united without condensation, one volume or atom of chlorine, for instance, uniting with one volume or atom of hydrogen, to form two volumes of hydrochloric acid, HCl. These two volumes constitute the molecule of hydrochloric acid, which is usually regarded as a chloro-derivative of the molecule of hydrogen, HH, and taken as a convenient standard of comparison for two-volume molecules in general.

The metals lithium, sodium, potassium, rubidium, cæsium, and silver are correlative to the above halogen elements, and accordingly may be looked upon as basylous or electro-positive varieties of hydrogen. Their received atomic weights, namely, Li 7, Na 23, K 39, Rb 85, Cs 133, and Ag 108, express the relative quantities of each of them which can displace 1 part by weight of hydrogen to unite with 35·5 parts by weight of chlorine. Now it is found by experiment that 7 parts of lithium, 23 parts of sodium, 39 parts of potassium, and 108 parts of silver have substantially the same specific heat as one another; so that 7 parts of lithium and 108 parts of silver, for instance, absorb or evolve the same amount of heat in undergoing the same increment or decrement of temperature. The specific heats of the atomic proportions of these four metals, and by analogy of rubidium and cæsium also, are moreover substantially identical with the specific heats of the atomic proportions of chlorine, bromine, and iodine, and may be expressed with sufficient accuracy for our present purpose by the number 6·2, in comparison with the specific heat of water taken as the standard of unity. Each of these metals unites with chlorine in but a single definite proportion, to form a chloride expressible by the general formula $M'Cl$, derivable from the type HCl; and the specific heats of these several chlorides and of the corresponding bromides and iodides, approximate to the number 12·4, giving a specific heat of 6·2 for each atom in the molecule.

The chlorides of the monad metals, though more or less volatile at high temperatures, are not sufficiently so to allow of their densities in the vaporous state being ascertained by experiment. Their theoretical vapour-densities, however, are assumed to be the halves of their respective atomic weights, and their molecules are accordingly referred to the normal two-volume standard. One or two of these metals, more particularly lithium and sodium, have been made to combine with the organic radicles methyl and ethyl; but the resulting methides and ethides have not been obtained in an isolated condition, and *à fortiori* have not had their vapour-densities determined.

The metals of this group have the common property of forming sulphates which combine with sulphate of aluminium to produce a highly characteristic class of hydrated double salts, crystallising in octahedrons, and known by the generic name of the alums. They are also distinguished by their capability of forming acid and mixed salts of dibasic acids, and incapability of forming basic and mixed salts of monobasic acids, properties, however, which appertain to silver in only a limited degree. The metals potassium, rubidium, and cæsium form a definite sub-group, characterised by special properties. They are the most powerfully basylous or oxidisable of all the elements, and the intensity of their basylity increases in the order of their atomic weights. Their hydrates and sulphydrates are very soluble in water, forming powerfully caustic solutions. Their carbonates also are very deliquescent, soluble, and caustic compounds. Their chlorides are deliquescent and soluble, their sulphates sparingly soluble, and their platino-chlorides and acid-tartrates almost insoluble. Sodium is far less basylous than potassium, and lithium than sodium. The inferior oxidisability of sodium is well shown by its want of action on a strong solution of caustic soda, and by the facility with which it is produced and manipulated in the operations of modern metallurgy. Its hydrate and sulphydrate resemble those of potassium, but its carbonate is efflorescent, very moderately soluble, and scarcely at all caustic; while carbonate of lithium is almost insoluble, and the phosphate yet more so, like the carbonates and phosphates of the alkali-earth metals. Moreover, while carbonate of potassium is perfectly fixed in the fire, carbonate of sodium loses a small proportion, and carbonate of lithium a considerable proportion of carbonic anhydride; and again, the solution of chloride of lithium, though to a less degree than that of chloride of magnesium, is decomposed during evaporation, with loss of hydrochloric acid. Silver, although distinguished from most of the heavy metals by the perfect neutrality of its soluble salts, differs from the alkali-metals proper in its high specific gravity, its permanence in air, the insolubility of its chloride, &c., and in the indifference of its oxide and sulphide to the action of water. Nevertheless there seems to be a relationship between sodium and silver manifested by the isomorphism of their anhydrous sulphates, and in other ways. Bearing in mind also the general rule that the specific gravities of allied metals increase in the order of their atomic weights, the superior specific gravity of sodium over that of potassium may be taken to indicate its having a latent association with the heavy metals. The triad metals thallium and gold, in addition to their characteristic trichlorides, form protochlorides corresponding in their specific heats, insolubility, and general properties, to the above-mentioned protochloride of silver, whence the metals themselves may be regarded as being at the same time monatomic and triatomic.

Group II.—**Dyad Metals**; namely, **glucinum, magnesium, calcium, strontium, barium, zinc, cadmium,** and **mercury.** The metals of this class agree with those last considered in being more or less strongly basylous, but differ from them in a variety of other particulars. Of glucinum very little is really known, but its unascertained properties will be assumed to correspond generally with the known properties of magnesium. With the exception of mercury, which in addition to its normal chloride, or corrosive sublimate, forms an inferior chloride, or calomel, to be left out of consideration for the present, all the members of this group unite with chlorine in a single proportion only. With the atomic weights heretofore usually accorded to these metals, their chlorides would be represented as protochlorides by the general formula $M'Cl$ corresponding to HCl; but doubling their respective atomic weights as advocated more particularly by Wurtz and Cannizzaro, their chlorides must be represented as dichlorides, by the general formula $M''Cl^2$ corresponding to OCl^2, as shown below:

	HCl	OCl^2	
G 4·5	GCl	G̶Cl^2	G̶ 9
Mg 12	MgCl	M̶gCl^2	M̶g 24
Ca 20	CaCl	C̶aCl^2	C̶a 40
Sr 43·75	SrCl	S̶rCl^2	S̶r 87·5
Ba 68·5	BaCl	B̶aCl^2	B̶a 137
Zn 32·5	ZnCl	Z̶nCl^2	Z̶n 65
Cd 56	CdCl	C̶dCl^2	C̶d 112
Hg 100	HgCl	H̶gCl^2	H̶g 200

Several metals not belonging to this group form chlorides analogous to those above tabulated, just as the triad metals thallium and gold, form protochlorides analogous to protochloride of silver. The disputed formulæ of a few of them are appended for the sake of illustration:—

Cu 31·75	CuCl	C̶uCl^2	C̶u 63·5
Sn 59	SnCl	S̶nCl^2	S̶n 118
Pb 103·5	PbCl	P̶bCl^2	P̶b 207

The general principles on which the determination of atomic weights must logically depend, were discussed very fully in a previous article (*vide* ATOMIC WEIGHTS), which it may be observed was necessarily written long before the date of its publication. It was therein stated, that although in the author's opinion, the arguments in favour of doubling the atomic weights of the metals now under consideration, were not at that time sufficiently cogent to warrant the adoption of a hasty change in old established usages, yet that, the proposal being then of very recent introduction, it was not improbable that in course of time the objections to which it was liable would be more or less satisfactorily explained away, while further potential arguments might possibly be adduced in its support. And this is what has since actually taken place; for although the objections to the proposal cannot even now be regarded as altogether overcome, yet the arguments in its favour preponderate so largely as to leave no doubt whatever about the ultimate necessity for its adoption. Before considering *seriatim* the reasons for and against the proposed doubling of the atomic weights of these metals, it may be observed at starting, that, just as there are monatomic, diatomic, and triatomic chlorous elements, so should we expect to have monatomic, diatomic, and triatomic basylous elements or metals. It would, moreover, be extremely strange if while triad and tetrad metals are abundantly met with, there should exist only one or two well-known dyad metals. Again, just as among chlorous elements, the distinction between monatomic and triatomic atoms was recognised long before the distinction between monatomic and diatomic atoms, so is it natural that among basylous elements also, the distinction between monatomic and diatomic metals now proposed for adoption, should not be established until long after the distinction between monad and triad metals had been all but universally acknowledged.

α. **Atomic Heat.**—If we represent the chlorides tabulated above, as dichlorides, we find that the proportions of metal combined with two atoms of chlorine in their respective molecules have their specific heats expressed by the number 6·2, just as have the several proportions of metal united with one atom of chlorine in undisputed protochlorides, and the several proportions of metal united with three atoms of chlorine in undisputed trichlorides. But if we continue to regard the chlorides in question as protochlorides, the proportions of metal contained in their respective molecules will have only half the specific heat of the proportions of metal contained in the molecules of undisputed proto- and trichlorides. In other words, with the doubled weights and formulæ, the atoms of this group of metals will have the same specific heats, whereas with the old atomic weights they will have only half the specific heats, of the atoms of chlorous dyads, such as sulphur and selenium; of chlorous and basylous monads, such as bromine, iodine, sodium, and silver; and of chlorous and basylous triads, such as phosphorus, arsenic, thallium, and gold. Moreover the specific heats of their respective chlorides, &c., written as dichlorides, will agree with the specific heats of undisputed proto- and trichlorides in this particular, that, divided by the number of atoms in the molecule, they will all yield the constant 6·2. Thus the ascertained specific heat of corrosive sublimate $\text{Ħg}\text{Cl}^2$ $(200 + 35{\cdot}5 \times 2)$ is 18·67, which divided by 3, gives the quotient 6·22.

Objection.—The argument from atomic heat is admitted to have great force, though hardly sufficient to be absolutely decisive of the question, inasmuch as the atomic heats of the non-metals, boron, carbon, and silicon, are not under any circumstances more than half as great as the atomic heats of their metallic congeners. It being therefore impossible to accord the same specific heats to the atoms of all the elements, it is quite conceivable that the atomic heat of certain metals should differ from the atomic heat of the remainder, that magnesium and mercury, for instance, should have only half the atomic heat of sodium and silver. Then the molecule of chloride of mercury HgCl, for instance, would have the specific heat of its constituent atoms, $3{\cdot}1 + 6{\cdot}2 = 9{\cdot}3$; while the molecule of chloride of silver AgCl, would have the specific heat of its constituent atoms, $6{\cdot}2 + 6{\cdot}2 = 12{\cdot}4$.

β. **Molecular Volume.**—Mercuric chloride and mercuric ethide, if represented as dyadic by the formulæ ĦgCl^2 and ĦgEt^2 respectively, have the same molecular volume as the corresponding monadic compounds, hydric chloride HCl, and hydric ethide HEt, respectively, and as the corresponding triadic compounds, arsenic chloride AsCl^3, and arsenic ethide AsEt^3 respectively. The gaseous volumes of zinc-chloride and stannous chloride have not been ascertained, but the gaseous volumes of their corresponding ethides and methides agree with the ethide and methide of mercury, in the circumstance of their respective vapour-densities being the halves of their atomic weights, when they are represented as dyadic compounds, thus:

2 vols.	2 vols.	2 vols.
H Cl	$\text{Ħg}''\text{Cl}^2$	$\text{As}'''\text{Cl}^3$
HEt	$\text{Ħg}''\text{Et}^2$	$\text{As}'''\text{Et}^3$
EtCl	$\text{Ƶn}''\text{Et}^2$	$\text{B}'''\text{Cl}^3$
	$\text{S̶n}''\text{Et}^2$	$\text{B}'''\text{Et}^3$

In other words, the volatile chlorides and ethides of these metals, if represented as dyadic, will have the same molecular volume, whereas if represented as monadic they will have only half the molecular volume of undisputed protochlorides and trichlorides, protethides and triethides, &c.

Objection.—The above argument from molecular volume is considered to have rather less weight than that from atomic heat: for by according to chloride of mercury and its congeners the formulæ which bring their molecular volumes into accordance with the molecular volumes of chloride of hydrogen, chloride of oxygen, &c., we are forced to accord to the metals themselves, molecular volumes which are discordant with the molecular volumes of the elements, hydrogen and oxygen, &c., thus:

2 vols.	2 vols.		
HCl	H^2O''	$Cl^2\bar{H}g''$	2 vols.
HEt	Et^2O''	$Et^2\bar{H}g''$	
$EtCl$	Cl^2S''	$Et^2\bar{C}d''$	
HH	OO	$\bar{H}g\bar{H}g$	4 vols.
$ClCl$	SS	$\bar{C}d\bar{C}d$	
$BrBr$	$SeSe$	$\bar{Z}n\bar{Z}n$	

In other words, the proportions of mercury, of cadmium, and by analogy of zinc, which combine with two atoms of chlorine, or ethyl, or methyl, have double the gaseous volume of the proportion of hydrogen which combines with one atom of chlorine, or ethyl, or methyl, and consequently double the volume of the proportions of oxygen and sulphur respectively which combine with two atoms, and of the proportion of nitrogen which combines with three atoms of chlorine, or ethyl, or methyl. But just as the diatomic chlorous elements, oxygen and sulphur, have the same gaseous volume as, and not double the volume of, the monatomic chlorous elements, chlorine and bromine, so should we expect the diatomic basylous elements, mercury and cadmium, to have the same volume as, and not double the volume of, the monatomic basylous metalloïd, hydrogen. This objection has been partly met by comparing the molecules of mercury, cadmium, &c., not with the molecules of free oxygen, free sulphur, &c., which are divisible in the act of combination, but with the molecules of the diatomic compound radicles carbonic oxide, sulphurous anhydride, ethylene, &c., which are indivisible; thus:—

2 vols.	2 vols.	2 vols.
$\overset{\prime}{H}{}^2$	$\bar{H}g''$	$O''Cl^2$
$\overset{\prime}{Cl}{}^2$	$\bar{C}d''$	$S''Cl^2$
$\overset{\prime\prime}{O}{}^2$	$(CO)''$	$\bar{H}g''Cl^2$
$\overset{\prime\prime}{S}{}^2$	$(SO^2)''$	$\bar{C}d''Cl^2$
$\overset{\prime\prime}{Se}{}^2$	$(C^2H^4)''$	$(CO)''Cl^2$
$\overset{\prime\prime\prime}{N}{}^2$	$(C^6H^6)''$	$(C^2H^4)''Cl^2$

Whatever value may be accorded to this explanation, however, the experimental discordance undoubtedly remains, that the atomic proportions of the dyadic basyloids mercury and cadmium, have double the volume of the dyadic chloroids oxygen and sulphur.

γ. Double Salts.—The characteristic property of a dyad element is its capability, when united with one and the same monatomic radicle, of parting with that radicle by two successive substitutions, and of thereby uniting with two distinct monatomic radicles. Now this property of combining with two different radicles is certainly very well exemplified by the class of metals we are at present considering, as shown in the list of compounds tabulated below, which might be largely extended:

$(HgCl)^2$	Mercury, dichloride	$\bar{H}g''Cl^2$
$HgCl.HgEt$	„ chlor-ethide	$\bar{H}g''ClEt^2$
$(HgEt)^2$	„ diethide	$\bar{H}g''Et^2$
$HgEt.HgMe$?	„ etho-methide	$\bar{H}g''EtMe$?
$ZnEt.ZnI$	Zinc iodo-ethide	$\bar{Z}n''EtI$
$CaCl.CaClO$	Bleaching powder	$\bar{C}a''Cl.ClO$
$SrNO^3.SrC^2H^3O^2$	Strontium acetato-nitrate	$\bar{S}r''NO^3.C^2H^3O^2$
$BaNO^3.BaC^2H^3O^2$	Barium acetato-nitrate	$\bar{B}a''NO^3.C^2H^3O^2$
$CuHO.CuF$	Copper, fluo-hydrate	$\bar{C}u''HO.F$
$PbHO.PbNO^3$	Lead, hydrato-nitrate	$\bar{P}b''HO.NO^3$
$PbHO.PbC^2H^3O^2$	„ hydrato-acetate	$\bar{P}b''HO.C^2H^3O^2$

The greater number of these double compounds possess a moderate degree of stability, while some of them, as the double halogen ethides and methides, are among the most definite and stable of metallic salts. The relation of the organic compounds of mercury and arsenic to one another is evidently parallel to that of alcohol and ether to the ethylamines, as shown below:

Triads.		Dyads.		Monads.	
$\mathrm{H^3N}$	$\mathrm{Cl^3As}$	$\mathrm{H^2O}$	$\mathrm{Cl^2Hg}$	HCl	ClNa
$\mathrm{EtH^2N}$	$\mathrm{EtCl^2As}$	EtHO	EtClHg	EtCl	EtNa
$\mathrm{Et^2HN}$	$\mathrm{Et^2ClAs}$	$\mathrm{Et^2O}$	$\mathrm{Et^2Hg}$		
$\mathrm{Et^3N}$	$\mathrm{Et^3As}$				

Again, just as in alcohol the basylous radicles, hydrogen and ethyl, are held together by diatomic oxygen, so in the hydrato-nitrate of lead the two chlorous radicles are held together by diatomic lead (Williamson, Chem. Soc. J. xvii. 211). Accordingly, if in alcohol we replace diatomic oxygen by monatomic chlorine, we get two distinct chlorides, thus:

$$\mathrm{PCl^3Cl^2} + \mathrm{HEtO''} = \mathrm{PCl^3O''} + \mathrm{HCl} + \mathrm{EtCl}.$$

And similarly, if in our lead-salt we replace diatomic lead by monatomic silver, we get two distinct argentides, thus:

$$\mathrm{SO^4Ag^2} + \mathrm{HO.NO^2Pb''} = \mathrm{SO^4Pb''} + \mathrm{HOAg} + \mathrm{NO^3Ag}.$$

Objections.—The force of this argument is much diminished by remembering that certain undoubted monatomic elements and groupings have the property, though to a limited extent, of combining with two distinct monatomic radicles. Chlor-ethide of mercury, for instance, $\mathrm{Hg''EtCl}$, may be written $\mathrm{(Hg^2)EtCl}$, and compared with iodo-nitrate of silver, $\mathrm{(Ag^2)I.NO^3}$, argento-chloride of sodium, $\mathrm{(Cl^2)AgNa}$, hydrofluoride of potassium, $\mathrm{(F^2)HK}$, hydro-acetate of potassium, $\mathrm{(2C^2H^3O^2)HK}$, and many similar compounds, in which we have the monatomic elements silver, chlorine, fluorine, as well as monobasic acetic acid, &c., combined with two different monatomic radicles, although, indeed, the stability of these compounds, save and except some of the hydrofluorides, is of a very feeble character. Moreover, in contrasting the properties of monatomic ethyl and diatomic ethylene, and comparing the undisputed monad metals with the former, and the metals under discussion with the latter, there is one point, at any rate, of some importance in which the comparison does not hold good. The hydrogen of a dibasic acid is found to be replaceable by two different monatomic radicles, and by the same radicle at two successive stages, whereas it is replaceable by a single diatomic radicle only, and that at a single operation. Thus the diatomic radicle ethylene may be substituted for the hydrogen of oxalic acid to form oxalate of ethylene, $\mathrm{(C^2H^4)''C^2O^4}$, which is the only derived oxalate of ethylene hitherto known; but with the monatomic radicle ethyl we have acid oxalate of ethyl, $\mathrm{(C^2H^5)HC^2O^4}$, neutral oxalate of ethyl, $\mathrm{(C^2H^5)^2C^2O^4}$, potassic oxalate of ethyl, $\mathrm{(C^2H^5)KC^2O^4}$, &c. In other words, the monatomic radicle ethyl does, and the diatomic radicle ethylene does not, form acid and double ethers or salts of dibasic acids; and a similar difference of behaviour is manifested by monatomic and diatomic chlorous radicles, such as acetyl $\mathrm{(C^2H^3O)'}$ and oxalyl $\mathrm{(C^2O^2)''}$, in their relation to a diacid base such as glycol. Now there certainly does not seem to be any decided difference in this particular between the two groups of metals. One member, at any rate, of the first group—namely, silver—does not or scarcely does, while several of the members of the second group very readily do, form well-defined acid and double salts, as exemplified by the acid oxalate of barium, $\mathrm{BaHC^2O^4}$, potassio-oxalate of zinc, $\mathrm{ZnKC^2O^4}$, acid carbonate of magnesium, $\mathrm{MgHCO^3}$, gay-lussite, $\mathrm{CaNaCO^3}$, dolomite, $\mathrm{MgCaCO^4}$, acid sulphate of zinc, $\mathrm{ZnHSO^4}$, glauberite, $\mathrm{CaNaSO^4}$, acid selenite of calcium, $\mathrm{CaHSeO^3}$, &c. &c. Such salts as the sulphovinates of calcium and barium cannot properly be adduced in illustration, because, although for some purposes, sulphovinic acid may be regarded as a double sulphate of ethyl and hydrogen, comparable with acid sulphate of potassium, yet it is in reality a conjugated compound analogous to the sulphamic and sulphophenic acids, for instance, and consequently as much monobasic as the formic, acetic, and nitric acids themselves.

It cannot, however, be contended in any way that the property of forming acid and double salts with dibasic acids is incompatible with the diatomic character of the metals forming them; for, indeed, there is no sufficient reason why the atom of a dyad metal should not bind together two atoms of dibasic sulphuric acid, for instance, just as we believe the diatomic radicle sulphuryl binds together two atoms of dihydric water, thus:—

$$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\qquad \left.\begin{matrix}\mathrm{H}\\(\mathrm{SO}^2)''\\\mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\qquad\qquad \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{SO}^4\qquad \left.\begin{matrix}\mathrm{H}\\\mathrm{Zn}''\\\mathrm{H}\end{matrix}\right\}\begin{matrix}\mathrm{SO}^4\\\mathrm{SO}^4\end{matrix}$$
$$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}\qquad\qquad\qquad\qquad\qquad \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{SO}^4$$

The utmost that can be said is, that the difference of properties exhibited by ethylene and ethyl in their behaviour with dibasic acids, is not paralleled by a corresponding difference of properties manifested under similar circumstances by members of the two groups of metals.

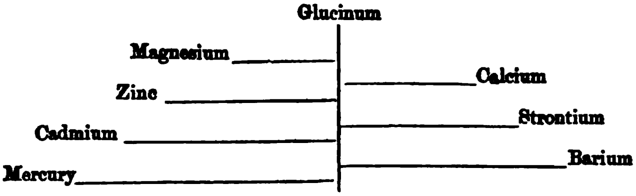
8. **Basic salts.**—A well-marked distinction between monatomic and polyatomic radicles, which has been pointed out more especially by Wurtz, results from the special tendency which the oxides of polyatomic, and particularly diatomic radicles have, to produce basic and anhydro-salts; or, as Wurtz expresses it, from the power which they have of accumulating in combination, and of thereby forming compounds containing multiple radicles, and belonging to types of greater and greater complexity. Thus we are acquainted with potassic monochromate, $K^2O(CrO^2.O)$, potassic anhydro-dichromate, $K^2O(CrO^2.O)^2$, and potassic anhydro-trichromate, $K^2O(CrO^2.O)^3$. Again, we have monethylenic glycol, $(C^2H^4.O).H^2O$, diethylenic glycol, $(C^2H^4.O)^2.H^2O$, triethylenic glycol, $(C^2H^4.O)^3.H^2O$, and tetrethylenic glycol, $(C^2H^4.O)^4.H^2O$, &c. This distinction, unlike those hitherto considered, is simply a matter of observation. We observe that diatomic oxides do, and monatomic oxides do not, as a general rule, accumulate in the manner above exemplified; but we see no reason why such a difference of behaviour should result from the different atomicities of the radicles. On this account therefore, that it is based on a difference of behaviour not directly deducible from difference of constitution, we can scarcely attach so much importance to this last distinction as to those which have been previously discussed. At the same time, the different habit of monatomic and diatomic radicles in this particular is very well marked. We are acquainted, for instance, with super-basic hydrates, chlorides, and acetates of ethylene, but with no super-basic hydrates, chlorides, or acetates of ethyl. The question consequently arises, whether a similar difference subsists between the alleged diatomic and the undisputed monatomic metals; and the answer, that such a difference does exist, is certainly, so far as it goes, in favour of the diatomicity of the metals now under consideration. Thus we can parallel some of the basic hydrates, chlorides, acetates, &c. of ethylene by similar compounds of calcium, magnesium, zinc, lead, copper, &c., but not by any compounds of the undoubtedly monad metals. We have, for example, Schaffner's hydrate of lead, $H^2O(\bar{P}bO)^2$; Payen's hydrate of lead, $H^2O(\bar{P}bO)^3$; Mendipite, $\bar{P}bCl^2.(\bar{P}bO)^2$; Atacamite, $\bar{C}uCl^2(\bar{C}uO)^3$; Schindler's oxychloride of zinc, $\bar{Z}nCl^2(\bar{Z}nO)^3.2H^2O$; Rose's oxychloride of calcium, $\bar{C}aCl^2(\bar{C}aO)^3.16H^2O$; hydromagnesite, $(\bar{M}gCO^3.H^2O)^3.\bar{M}gH^2O^2$; dibasic acetate of copper, $C^4H^6\bar{C}uO^4.\bar{C}uO.3H^2O$; dibasic acetate of lead, $C^4H^6\bar{P}bO^4.\bar{P}bO.3H^2O$; tribasic acetate of copper, $C^4H^6\bar{C}uO^4(\bar{C}uO)^2$; tribasic acetate of lead, $C^4H^6\bar{P}bO^4(\bar{P}bO)^2.3H^2O$; Mitscherlich's dibasic nitrate of mercury, $\bar{H}gN^2O^6.\bar{H}gO.2H^2O$, &c. &c. This is perhaps a suitable place for referring to an observation of Wurtz, to the effect that, by representing the metals of this group as diatomic, we are able to express the simple molecules of their several salts, with entire instead of with half atoms of water of crystallisation, as illustrated by the following among many other examples: acetate of copper, $C^4H^6\bar{C}uO^4.H^2O$; acetate of lead, $C^4H^6\bar{P}bO^4.3H^2O$; perchlorate of lead, $\bar{P}bCl^2O^8.3H^2O$; nitrate of copper, $\bar{C}uN^2O^6.3H^2O$; chloride of nickel, $\bar{N}iCl^2.9H^2O$, &c.

Objections.—It is contended that the property of accumulating in combination is not necessarily but only accidentally associated with polyatomicity, and that, just as the acetic and iodic anhydrides form anhydro-salts, such as $(C^2H^3KO^2)^2.C^4H^6O^3$ and $KIO^3.I^2O^5$, without prejudice to their monatomicity, so may the plumbic and cupric base-oxides form basic salts without prejudice to their monatomicity. From several considerations, however, the existence of a diacetic acid $C^4H^8O^4$, and a trihydric iodic acid, H^3IO^4, seems not improbable; and if so, the anhydro-acetates and anhydro-iodates may be associated in reality with the polybasic forms of their respective acids. As for the argument from water of hydration, taken by itself, it certainly cannot lay claim to any great weight, since there is no more obvious reason why one atom of water should not combine with two atoms of salt, H^2O with $(C^2H^3CuO^2)^2$ for instance, than there is why one atom of salt should be able to combine with two or three atoms of water.

But although the arguments in favour of regarding the zinco-calcic group of metals as dyadic, when taken separately, are open to the objections above pointed out, yet taken altogether, they seem to present so great a preponderance of evidence in support of the proposal, as to render its adoption almost a matter of necessity. Accepting this conclusion, then, as inevitable, and according to the above metals the doubles of their previously received atomic weights, we are at once struck by the very obvious parallelism subsisting between them and the already considered monad metals, as shown below:—

Li'	7	G''	9				
Na'	23	Mg''	24	K'	39	Ca''	40
—		Zn''	65	Rb'	85	Sr''	87·5
Ag'	108	Cd''	112	Cs'	133	Ba''	137
		Hg''	200				

The metals of the alkaline-earth sub-group, namely, calcium, strontium, and barium, are scarcely less basylous or oxydisable than those of the alkalis, and the degree of their basylity also increases in the order of their atomic weights. Their hydrates and sulphydrates, like those of the alkali-metals, are soluble in water, forming caustic solutions which absorb carbonic anhydride with great avidity, to form, however, insoluble carbonates; and their sulphates are likewise insoluble. Among the members of the other sub-group, the manifestation of metallic properties, as popularly understood, rather than of basylous characters, increases in the order of their atomic weights; and accordingly we may regard the upper members of each sub-group as exhibiting a very general form, and the lower members as exhibiting highly specialised forms of the metallic character, and may figure the difference to ourselves in some such diagram as the following:—



The metals of the less basylous or more reguline sub-group are distinguished by their volatility, which increases in the order of their several atomic weights. The hydrates of these metals are insoluble in water, and only those of glucinum and magnesium manifest much affinity for carbonic anhydride. The sulphides of zinc, cadmium, and mercury are insoluble permanent precipitates, while that of magnesium also appears to be insoluble in, though readily decomposible by water. Their sulphates, unlike those of the more basylous dyads, are all soluble in water, with the exception of sulphate of mercury, which is decomposed thereby into sulphuric acid and a basic salt. In many points of its behaviour, magnesium presents a general resemblance to calcium, and was at one time classified with the alkaline-earth metals.

In addition to corrosive sublimate, $HgCl^2$, mercury forms an inferior chloride, or calomel, whose molecule may be represented by the formula $HgCl$, corresponding to that of proto-chloride of silver, $AgCl$, or by the formula Hg^2Cl^2, corresponding to that of subchloride of sulphur S^2Cl^2; and the selection of one or other of these expressions will of course determine the entire series of formulæ to be accorded to the entire series of mercurous salts. The formula $Hg'Cl$, by which calomel is represented as a protochloride of mercurosum, is recommended by its superior simplicity, by the ready susceptibility of mercurous salts to double decomposition without change of type, by the resemblance of calomel to the insoluble monad chlorides of silver, gold, &c., and by the determination of its vapour-density, which is found to be $\frac{200 + 35\cdot5}{2} = 117\cdot75$; so that two volumes of calomel vapour, $HgCl$, contain one volume of chlorine, just as two volumes of hydrochloric acid, HCl, contain one volume of chlorine. On the other hand, the formula Hg^2Cl^2 is recommended by its consistency with the law of even numbers, which declares that a dyad element can never unite with an uneven number of monad atoms, and with the frequent spontaneous decomposition of mercurous salts into mercuric salts and mercury, $Hg^2Cl^2 = HgCl^2 + Hg$. Moreover, the existence of several basic mercurous compounds is opposed to the representation of normal mercurous compounds as proto-salts; while the discordance in molecular volume between calomel and subchloride of sulphur, as revealed by the determination of their vapour-densities ($S^2Cl^2 = 2$ vols., while $Hg^2Cl^2 = 4$ vols.), may be explained by supposing that the vapour of calomel, like that of many other salts, undergoes what is known as dissociation (i. 469; ii. 816) into two volumes of mercuric chloride, $HgCl^2$, and two volumes of mercury, Hg. This supposition is to some extent warranted by the observation, that calomel vapour amalgamates gold leaf, and that corrosive sublimate may be detected in resublimed calomel (Chem. Soc. J. xvii. 421). In the present undecided state of the question, however, it seems preferable, as a mere matter of convenience, to employ habitually the simpler series of formulæ for calomel and mercurous salts in general.

GROUP III. **Triad Metals.**—Classifying the metals according to their maximum atomicities, there are only three triad metals properly so called, namely, **aluminium, thallium, and gold**: for the trichlorides of arsenic, antimony, and bismuth must be regarded as the inferior chlorides of pentad, just as the protochlorides of thallium and gold are the inferior chlorides of triad elements. The formula for thallic chloride, $TiCl^3$, and the atomic weight for thallium, 203, have not at any time been disputed. Auric chloride was formerly represented as a sesquichloride by the formula Au^2Cl^3, the atomic weight of gold being taken as 98; but it is now always represented as a trichloride by the formula $AuCl^3$, the atomic weight of the metal being fixed at 196. The old sesquiatomic formula for aluminic chloride, Al^2Cl^3, in accordance with which the atomic weight of aluminium was taken as 13·75, though still in very general use, cannot now be defended on any rational grounds whatever. It is admitted on all hands that the smallest proportion of aluminium found to exist in any definite compound is 27·5 parts, and that this proportion is indivisible or atomic throughout all the reactions which aluminic compounds undergo. Evidently, therefore, it ought to be represented as indivisible or atomic by the symbol Al''' or All''', and not as dipartite by the symbol Al^2. Regarded as triadic, with the atomic weights 27·5, 203, and 196·5 respectively, it is found that the specific heats of the atoms of aluminium, thallium and gold approximate to the number 6·2, and are accordingly identical with the specific heats of the atoms of monad metals, such as sodium and silver, of dyad metals such as magnesium and mercury, of tetrad metals such as tin and lead, and of pentad metals such as arsenic and antimony, &c. The trichlorides of thallium and gold are decomposed by heat, with evolution of chlorine; but aluminic chloride volatilises unchanged, and its vapour-density has been found by Deville to accord, not with the molecular formula $AlCl^3$, but with the more complex expression Al^2Cl^6; and many chemists attach so much importance to this determination, that they habitually represent aluminium as a triatomic element by the symbol $All^{vi} = 55$. But from some unpublished experiments of Mr. Buckton and the author of this article, it appears that the vapour-densities of aluminic methyl and ethyl accord unmistakeably with the molecular formulæ $AlMe^3$ and $AlEt^3$ respectively. Aluminium-methyl certainly is, and aluminic chloride not improbably may be, a body of the same class as formic acid, acetic acid, boric methide, sulphur, selenium, &c., whose vapours require to be heated very far above the boiling points of the several liquids before acquiring their normal molecular volumes. Thus, at 220° and all superior temperatures, the corrected vapour-density of aluminium-methyl is perfectly constant, and accords with the formula $AlMe^3$; but below 220° its corrected density increases at a very rapid rate, so as to become nearly doubled at 130°, which high density would of course accord approximatively with the formula Al^2Me^6. Bearing in mind, however, the rule deducible from the separate experiments of Deville and Cahours, that the molecular formula of a body is to be calculated from its permanent or ultimate, and not from its variable or initial vapour-density, and having regard also to the ascertained behaviour of the vapour of aluminic methide, the only observed vapour-density of aluminic chloride cannot, in the author's opinion, be taken to authorise the recognition of aluminium as hexatomic and the representation of its chloride by the formula $All^{vi}Cl^6$, or Al^2Cl^6. By adopting the formula $AllCl^6$, we should have to accord to aluminium an atomic heat twice as great as that of any other metal, while by adopting the formula Al^2Cl^6, we should systematically represent an indivisible proportion by a divisible symbol, which is absurd: for the proportion of aluminium contained in the molecule of aluminic chloride, is admittedly the smallest proportion of aluminium that is contained in the molecule of any aluminic compound whatsoever. There are, moreover, other objections: for if aluminium were really hexatomic, it would differ from all other elements known to chemists in its inability to form a proto-, di-, tri-, or tetra-chloride. Again, while the existence of such salts as the alums, $K'Al'''(SO^4)^2$, derived from $2H^2SO^4$, is a necessary consequence of the triatomicity of aluminium, their constitution would be scarcely explicable at all on the assumption of its hexatomicity. Lastly, the circumstance that certain aluminic compounds present a marked resemblance in composition and properties to similar undoubted triatomic compounds of other elements, as of boron and antimony, for instance, is at any rate somewhat opposed to the notion of aluminium having in reality a hexatomic character. Boron would seem to stand to aluminium in much the same relation as that in which lithium stands to sodium, and glucinum to magnesium. In each pair of elements the basylity of the second is superior to that of the first term; while the monadic are more basylous than the corresponding dyadic, and these again more basylous than the corresponding triadic elements. Boric and aluminic hydrates alike act either as feeble acids or feeble bases. The isomorphous borate and aluminate of magnesium, or boracite and spinelle, though both subject to a considerable range of composition, are referrible to the similar formulæ MgB^2O^4 and $MgAl^2O^4$, respectively. As before remarked, however, the specific heat of the atom of boron is anomalous.

Thallium would appear to occupy among the triad metals a position similar to that of mercury among the dyads; but the position of gold in this group, whatever that position may be, is without obvious parallel. In addition to their trichlorides, &c., thallium and gold each form a protochloride and a well-defined series of monad salts. The similarity of several of the monad salts of thallium to the corresponding compounds of potassium is very marked. Thus its chloride produces an insoluble double salt with chloride of platinum; its acid tartrate occurs as a crystalline precipitate; its sulphate forms with sulphate of aluminium a well characterised alum; while its hydrate is readily soluble in water, forming a caustic solution which absorbs carbonic anhydride from the air. On the other hand, protosulphide of thallium, like that of silver, constitutes a dense black precipitate. Again, protochloride of thallium, though more soluble in water, has a general resemblance to chloride of silver, while the protobromides and iodides of the two metals present even a greater degree of similarity. The most stable of the monad salts of gold is the soluble crystalline sodio-sulphide, $AuNaS.4H^2O$. The protoxide is very unstable, and the protochloride is known only as an insoluble residue.

GROUP IV. **Tetrad Metals**; including **tin, lead, titanium, zirconium, thorinum,** and **tantalum.**—These metals are associated with the non-metallic tetrads carbon and silicon, just as the triad elements aluminium and boron are associated with one another. The tetrad elements agree with those of the monad and dyad groups in being divisible into a more especially reguline, and a more especially basylous subgroup, the lower members of each of which possess the respective distinctive characters of the sub-group in their greatest intensity. The relations of the members of the first five groups to one another is shown in the following table:—

Monads.		Dyads.		Triads.		Tetrads.		Pentads.	
Li	7	Gl	9	Bo	11	C	12	N	14
Na	23	Mg	24	Al	27·5	Si	28	P	31
,,	. .	Zn	65	,,	. .	,,	. .	As	75
Ag	108	Cd	112	,,	. .	Sn	118	Sb	122
,,	. .	Hg	200	Tl	203	Pb	207	Bi	210
K	39	Ca	40	,,	. .	Ti	48	,,	. .
Rb	85	Sr	87·5	,,	. .	Zr	89·5	,,	. .
Cs	133	Ba	137	,,	. .	,,	. .	,,	. .
						Th	231		

The tetrahydric character of marsh gas has been recognised from almost the earliest days of organic chemistry, but the now received formula CH^4, in which the carbon is represented as indivisible or atomic, was first introduced by Gerhardt in 1842, instead of the previously employed formula C^2H^4, in which the carbon was unwarrantably represented as dipartite. The tetratomicity of tin and silicon was first advocated by the author in 1857 and the following years (Phil. Mag. xiii. 434, and xviii. 368; Rep. Brit. Assoc. 1858, p. 58), and was definitively established by the separate researches of Cahours on the stannethyls in 1860 (Ann. Ch. Phys. [3] lviii. 5), and of Friedel and Crafts on the organic compounds of silicon (Bull. Soc. Chim. 1863, p. 174). The tetratomicity of titanium, zirconium and tantalum follows as a matter of course from the observed vapour-densities of their chlorides, and similarly that of lead from the vapour-density of its ethylide, though it is believed that this is the first occasion on which lead has been definitely classified as a tetratomic element, in association with tin rather than with calcium. The chlorides of carbon, silicon, tin, titanium, zirconium, and tantalum, represented as tetrachlorides by the general formula $M''''Cl^4$, and the ethylides of silicon, tin, and lead, represented by the general formula $M''''Et^4$, have vapour-densities which are the halves of their respective atomic weights, and accordingly have the same molecular volume as the protochloride of hydrogen HCl, the dichloride of mercury $HgCl^2$, and the triethylide of aluminium $AlEt^3$, &c. Moreover, the chlorine of the chlorides of carbon, silicon, and more especially of tin, is found to be experimentally replaceable at four successive stages. Thus, we have $SnCl^4$, $SnCl^3Et$, $SnCl^2Et^2$, $SnClEt^3$ and $SnEt^4$, corresponding to CCl^4, CCl^3H, CCl^2H^2, $CClH^3$, and CH^4, respectively, and so on. Again with the tetrad atomic weights 118 and 207, the metals tin and lead have the normal atomic heat which is expressed more or less closely by the number 6·2. The specific heats of the other metals of this group have not been ascertained, but the specific heats of carbon and silicon among the tetrad elements, like that of boron among the triad elements, must, according to our present imperfect knowledge, be regarded as exceptional or anomalous.

Tetrachloride of tin is a colourless fuming liquid, which combines with water to form a series of crystalline soluble salts. Tetrachloride of lead is known only in the form of hydrated crystals. It is made by treating peroxide of lead PbO^2, with cold aqueous hydrochloric acid, when solution takes place without effervescence, and on evaporation in vacuo, crystals of the tetrachloride separate out, together with much dichloride of lead. The solutions of the tetrachlorides of tin and lead are decomposed by alkalis, with precipitation of the respective peroxides, and by sulphuretted hydrogen, with precipitation of the respective persulphides, the former of a pale yellow, the latter of an orange-red colour. The dichlorides of tin and lead, which have been incidentally referred to when discussing the dyad metals, are readily fusible, volatile solids, whose solutions, like those of the tetrachlorides, are decomposed by alkalis, with precipitation of their respective protoxides, and by sulphuretted hydrogen, with precipitation of their respective protosulphides, the former of a dark brown, and the latter of a black colour. It may be here observed that the property of forming insoluble sulphides, not readily decomposed by water, constitutes a useful distinguishing character between the reguline and alkaligenous sub-groups of metals belonging to each of the primary groups, this property being manifested by silver, zinc, cadmium, mercury, thallium, tin, lead, arsenic, antimony and bismuth, but not by potassium, cæsium, rubidium, calcium, strontium, barium, titanium, zirconium, thorinum and tantalum, or yet by the metals yttrium, cerium, lanthanum, and didymium, to which we shall presently refer more particularly. Many of the dyad salts of reguline lead, however, present a marked resemblance in properties to the similar salts of the alkali-earth metals, and are frequently isomorphous with them, just as the monad salts of reguline thallium correspond with the similar salts of potassium. On the other hand, an almost special characteristic of lead, and one strongly corroborative of its polyatomicity, consists in its very marked tendency to form double and superbasic salts with monatomic radicles. Lead differs also from its congener, tin, in the greater degree of its basylity, or power of neutralising even feeble acids; while a further difference between them results from the superior stability of the di-salts over the tetra-salts of the one metal, and of the tetra-salts over the di-salts of the other.

The less reguline sub-group of tetrad metals, namely, titanium, zirconium and thorinum, are associated with silicon and tin by the isomorphism of rutile, TiO^2, and artificial thorina, ThO^2, with native tinstone SnO^2 (Nordenskiöld and Chydenius, Pogg. Ann. cx. 642), and by the vapour-densities of titanic and zirconic chlorides, $TiCl^4$ and $ZrCl^4$, corresponding with that of stannic chloride, $SnCl^4$. The sulphides of titanium, zirconium and thorinum are not producible in the moist way. Their oxides are hard crystalline bodies unattackable by ordinary acids, save the hydrofluoric. Their hydrates occur as white gelatinous precipitates, which dissolve readily in acids, to form more or less definite salts. Just as the hydrates of the dyad alkaline-earth metals, $M''H^2O^2$, are less soluble and basylous than those of the monad alkali-metals, so should we expect the hydrates of the unrecognised triad earth-metals, $M'''H^3O^3$, to be less soluble and basylous even than those of the dyads, and the hydrates of the non-reguline tetrad metals, $M''''H^4O^4$ or $M''''H^2O^3 (= M''''H^4O^4 - H^2O)$, to be still less so. In other words, we should be prepared to find, in the sub-group of tetrad metals we are now considering, but a very inferior degree of basylity, more especially in the superior members of the sub-group, seeing that the degree of basylity habitually increases in the order of the atomic weights of the consecutive metals. We accordingly find that the characters of hydrated titania are fully as much acid as alkaline, though we are nevertheless acquainted with sulphates, nitrates, phosphates and even a potassio-carbonate of titanium. But the basylity of zirconia is far better marked. Its silicate constitutes zircon; its carbonate is formed by precipitation; its sulphate is a soluble crystalline salt; while its potassio-sulphate is thrown down as a crystalline precipitate on mixing solutions of the separate sulphates of potassium and zirconium. Thorinum forms a large number of well-defined salts, including a potassio-sulphate corresponding to that of zirconium in its character and mode of formation. Moreover, hydrated thorina is sufficiently basylous to expel ammonia from sal-ammoniac, and to absorb carbonic anhydride from the atmosphere. Tantalum, which agrees with the above elements in not yielding a precipitable sulphide, and in many other particulars, and whose atomic weight, 138, would induce us to assign it a position between zirconium and thorinum, differs from both of them in several important properties. Thus its chloride is decomposed by water, with separation of tantalic hydrate, which, instead of being less acidulous than hydrate of zirconium, is apparently more acidulous even than hydrate of titanium.

This seems a fitting place at which to make a few observations upon some of the rarer metals. Indium, which is especially characterised by the indigo-blue band appearing in its spectrum, is, according to the account of its discoverers, Messrs. Reich and Richter, a very soft lustrous metal, permanent in air and water, and having a specific gravity of about 7·2. Its hydrate and carbonate constitute white precipitates, and its sulphide a yellow precipitate insoluble in acetic, but soluble in mineral acids, while its chloride may be obtained as a white crystalline sublimate. Its equivalent weight is about 37, and its atomic weight may accordingly approximate to 37, 74, 111, or 148, &c. Its properties are too imperfectly known to allow of its being referred satisfactorily to any particular family of elements, but it evidently belongs to the reguline division of the metals, and seems to have much the same relation to thallium that tin has to lead.

Columbium or niobium was discovered by Hatchett in 1801, and tantalum by Ekeberg in 1802; but Wollaston in 1809 reported that the two metals were identical, and his opinion was generally accepted until 1846, when H. Rose succeeded in distinguishing between them; but despite his admirable labours the chemistry of niobium continues to be in a very unsatisfactory state. It appears, however, that the element forms two volatile chlorides, a white infusible inferior chloride, and a yellow fusible superior one. To each of these chlorides there corresponds an oxide or anhydride, the inferior one having a specific gravity from 4·6 to 5·2, and the superior one a specific gravity from 5·5 to 6·7, that of tantalic anhydride being from 7·0 to 8·2. H. Rose found that one of the chlorides (? the inferior one) contained 24·4 parts of metal united with 35·5 parts of chlorine, and regarding this compound as a tetrachloride, the atomic weight of niobium would be 97·6. Deville has since ascertained the vapour-density of one of the chlorides (? the superior one), and found it to be 10·9, that of the only known chloride of tantalum being 9·6, corresponding very closely with its theoretical density calculated for the formula $TaCl^4$, namely 9·7 (Compt. rend. lvi. 891). Assuming the correctness of the atomic weight 97·6, the theoretical vapour-density of a hexachloride, $NbCl^6$, would be 11·7, which agrees more nearly than any other with the determination of Deville. If this formula be correct, niobium, and by analogy tantalum, must be regarded as hexatomic rather than as tetratomic metals. It is not improbable also that titanium ought to be classified with these metals, instead of with zirconium; and in connection with this point, it may be observed that the received atomic weight of niobium is almost exactly intermediate between those of titanium and tantalum.

The metals yttrium, cerium, lanthanum, and didymium possess the following properties in common with one another and with thorinum:—Their hydrates constitute gelatinous precipitates, which expel ammonia from sal-ammoniac solution, and absorb carbonic anhydride from the atmosphere. Their sulphides are not producible in the moist way, and their sulphates are precipitated by sulphate of potassium in the form of crystalline double salts. The equivalent weights of these four metals, which replace 1 pt. of hydrogen to unite with 35·5 pts. of chlorine, are Y 32, Ce 46, La 46, and Di 48, but what their atomic weights are is altogether undecided. In the present state of knowledge, their extreme basylity cannot any longer be regarded as inconsistent with their di-, tri-, or even tetratomicity, and there are some points in the behaviour of didymium, at any rate, which are suggestive of its being a triad element. Cerium is distinguished from lanthanum and didymium, as well as from yttrium, by the facility with which it forms a superior and feebly salifiable oxide.

GROUP V. **Pentad Metals.**—These are only three in number, namely arsenic, antimony, and bismuth, which are associated with the non-metals nitrogen and phosphorus, just as the tetrad metals tin and lead are associated with the non-metallic tetrads carbon and silicon. Although the pentatomicity of this group of elements is very well established, as shown by the phosphoric and arsenic acids, for instance, and their corresponding chlorides and oxides, as formulated below, yet it must be admitted that their more general and characteristic behaviour is triadic:

$$\begin{array}{llll}
P^{v}Cl^{5} & \left.\begin{matrix}P^{v}\\H'\end{matrix}\right\}O''^{3} & \left.\begin{matrix}P^{v}\\H'^{3}\end{matrix}\right\}O''^{4} & \left.\begin{matrix}P^{v}\\P^{v}\end{matrix}\right\}O''^{5} \\
As^{v}Et^{3}Cl^{2} & \left.\begin{matrix}As^{v}\\H'\end{matrix}\right\}O''^{3} & \left.\begin{matrix}As^{v}\\H'^{3}\end{matrix}\right\}O''^{4} & \left.\begin{matrix}As^{v}\\As^{v}\end{matrix}\right\}O''^{5}
\end{array}$$

In some cases, moreover, these elements form monad compounds. Thus, Griess has shown that, in a variety of organic bodies, a single atom of nitrogen may be substituted either for 1 or for 3 atoms of hydrogen. Phosphorus and its associated metals were formerly represented by atomic weights, the halves of those now universally adopted, and it is only within a very few years that the habit of writing the antimonious and bismuthous chlorides as sesquichlorides by the formulæ Sb^2Cl^6 and Bi^2Cl^6, respectively, has been completely abandoned; nor indeed is it very long since chloride of bismuth was frequently represented as a protochloride by the formula BiCl. It is only, however, with the atomic weights now employed, namely, P 31, As 75, Sb 122, and Bi 210, that the atoms of the four elements have approximately the standard specific heat of 6·2. The specific gravity of nitrogen gas being identical with its atomic weight, or with the half of its molecular weight, the two-volume molecule of nitrogen is represented by the expression $N'''N'''$, just as that of oxygen is represented by $O''O''$, and that of hydrogen by $H'H'$. Deville, however, has shown that the vapour-densities of phosphorus and arsenic are the doubles of their respective atomic weights, and that these densities when corrected, are unalterable by any increase of temperature, so that the two-volume molecules of phosphorus and arsenic have to be represented by the expressions P^4 and As^4. Williamson has very plausibly suggested that, while the molecule of nitrogen may be regarded as ammonia, $N'''H'^3$, in which the three atoms of monatomic hydrogen are replaced by one atom of triatomic nitrogen, $N'''N'''$, the molecules of phosphorus and arsenic may be regarded as phosphine and arsine, $P'''H'^3$ and $As'''H'^3$, in which the three atoms of monatomic hydrogen are replaced by three atoms of monatomic phosphorus and monatomic arsenic respectively, $P'''P'^3$ and $As'''As'^3$. Except that bismuth does not form a trihydride, the volatile trihydrides, triethylides, and trichlorides of these five elements all form two-volume molecules, while the hydrogen, ethyl, and chlorine of the respective compounds are readily replaceable in thirds at three successive stages. The majority of the pentad compounds dissociate or decompose at or below their boiling points; but the molecules of nitric acid $N^{v}H'O''^3$, oxychloride of phosphorus $P^{v}Cl'^3O''$, oxy-ethylstibine $Sb^{v}Et'^3O''$, &c., &c., have vapour-densities which are the halves of their atomic weights, and accordingly correspond with the normal two-volume standard. Arsenic, antimony, and bismuth differ from the majority of the metals in being destitute of malleability or tenacity, and are therefore very commonly described as brittle or semi-metals. Their reguline character is, however, very well marked, and their sulphides are easily formed by precipitation. The permanently reguline habit of arsenic, however, is less decided than that of its congeners; for finely powdered arsenic oxidises readily in moist or heated air, and its precipitated sulphide is slowly decomposed by ebullition with water. All three metals manifest both acid and basic properties, the former being shown most strikingly by arsenic and the latter by bismuth.

GROUP VI. **Hexad Metals.**—The metals characteristic of this group—namely **tellurium, molybdenum,** and **tungsten**—are but very imperfectly known. Their hexatomicity, however, appears to be established by the analogy subsisting between certain of their compounds and the similar hexatomic compounds of the non-metals sulphur and selenium, thus:

SCl^2O^2	. .	. .	$\cancel{Mo}Cl^2O^2$	$\cancel{W}Cl^2O^2$ & $\cancel{W}Cl^6$
SH^2O^4	SeH^2O^4	TeH^2O^4	$\cancel{Mo}K^2O^4$	$\cancel{W}H^2O^4$
SO^3	. .	TeO^3	$\cancel{Mo}O^3$	$\cancel{W}O^3$

With the atomic weights S 32, Se 79·5, Te 129, and $\cancel{W}$ 184, the specific heats of the atoms of sulphur, selenium, tellurium, and tungsten approximate to the number 6·2; while the specific heat of the atom of molybdenum, $\cancel{Mo}$ 96, has yet to be ascertained. The vapour-densities of the oxychloride and trioxide of sulphur are the halves of their respective atomic weights, and their molecules consequently accord with the normal two-volume standard. The corresponding compounds of molybdenum are also volatile, but at too high a temperature to allow of the ready determination of their vapour-densities; and the same remark applies to the hexachloride and oxychloride of tungsten. But trioxide of tungsten is fixed in the fire, while trioxide of tellurium decomposes into dioxide and free oxygen, as does indeed vaporised trioxide of sulphur at a red heat. The semi-metal tellurium is isomorphous with, and in its general characters and behaviour very closely resembles, the semi-metal antimony, the two elements obviously occupying analogous positions in the sulphur and phosphorus groups respectively. The exact position of molybdenum in relation to the sulphur-group proper is as yet undetermined. With an atomic weight much inferior, it exhibits metallic characters far more perfectly than tellurium, while its most characteristic compounds have just the constitution and general properties which those of a metallic analogue of the sulphur elements might be expected to present.

The association of tungsten with molybdenum, though scarcely established beyond question, is not improbably analogous to that of bismuth with antimony, tin with lead, &c., the difference in atomic weight between the several pairs of elements being almost identical. The trioxides of tellurium, molybdenum, and tungsten occur as insoluble powders, which have many properties in common, including a marked tendency to form anhydro-salts with the stronger bases, and a capability of acting as feeble bases to the stronger acids. Tungstic acid $\cancel{W}H^2O^4$, and its hydrate $\cancel{W}H^2O^4.H^2O$, have been described by Riche (Ann. Ch. Phys. [3] l. 5), but molybdic acid is not known in the isolated state, though its salts, formed on the type $\cancel{Mo}M^2O^4$, are very well defined. Graham, however, has recently obtained both molybdic and tungstic acids in the colloïd form, as perfectly soluble compounds possessed of considerable stability, having decidedly acid characters, and altogether closely resembling one another (Proc. Roy. Soc. xiii. 340). The trisulphides of molybdenum and tungsten are powerful sulphanhydrides, which combine with sulphide of potassium to form beautiful red and orange crystalline salts. The several elements now under consideration are not only hexatomic, but also tetratomic, and in some cases even diatomic, just as we have seen that the pentad elements are triatomic and even monatomic. Thus we have—

. .	$\mathrm{SCl^4}$	$\mathrm{SeCl^4}$	$\mathrm{TeCl^4}$	$\mathrm{\cancel{Mo}Cl^4}$	$\mathrm{\cancel{W}Cl^4}$
. .	$\mathrm{SO^2}$	$\mathrm{SeO^2}$	$\mathrm{TeO^2}$	$\mathrm{\cancel{Mo}S^2}$	$\mathrm{\cancel{W}S^2}$
$\mathrm{OH^2}$	$\mathrm{SH^2}$	$\mathrm{SeH^2}$	$\mathrm{TeH^2}$	$\mathrm{\cancel{Mo}Cl^2}$	. .
$\mathrm{OCl^2}$	$\mathrm{SCl^2}$	. .	$\mathrm{TeCl^2}$	$\mathrm{\cancel{Mo}O.}$	. .

The vapour-densities of the hydrides of oxygen, sulphur, selenium, and tellurium, and of the chlorides of oxygen and sulphur among the dyad compounds, as well as of dioxide of sulphur among the tetrad compounds, are the halves of their atomic weights; or their respective molecules correspond with the normal two-volume standard. Of the other compounds above tabulated, the protoxide of molybdenum, and the disulphides of molybdenum and tungsten, are not volatilisable, while the remainder, though volatile, have not had their vapour-densities determined. In a classification of elements according, not to their maximum, but to their most characteristic atomicities, oxygen, sulphur, and by consequence selenium and tellurium, would probably be regarded as dyadic.

GROUP VII. Heptad Metals.—The elements referred to at the commencement of this article under the head of non-metallic monads, namely chlorine, bromine, and iodine, have the property of forming, in addition to their respective mon-hydrides, well-marked triad, pentad, and even heptad compounds, examples of which last are afforded by their respective quadroxy-acids, $\mathrm{Cl^{vii}HO^4}$, $\mathrm{Br^{vii}HO^4}$, $\mathrm{I^{vii}HO^4}$, and $\mathrm{I^{vii\,2}O^7}$. Iodine, though in some sense the representative of tellurium and antimony, cannot rank even as a semi-metal, but we are acquainted with at least one perfect or malleable metal which forms similar heptad compounds, namely manganese. With the atomic weight 55, the atom of manganese has the same specific heat as the atoms of chlorine, bromine, and iodine, namely 6·2, and forms not only a well-defined acid of moderate stability, the permanganic acid $\mathrm{\cancel{Mn}^{vii}HO^4}$, whose potassium-salt, $\mathrm{\cancel{Mn}^{vii}KO^4}$, is isomorphous with perchlorate of potassium, $\mathrm{Cl^{vii}KO^4}$, but also a corresponding volatile heptachloride $\mathrm{\cancel{Mn}^{vii}Cl^7}$. The general properties of manganese, however, will be more appropriately considered in the next section devoted to the iron family of metals. The succeeding table of chlorides, hydrides, and hydrates is not without interest as exhibiting the characteristic atomicities of the different groups of elements:—

$\mathrm{Li'Cl}$	$\mathrm{\cancel{G}''Cl^2}$	$\mathrm{B'''Cl^3}$	$\mathrm{C''''H^4}$	$\mathrm{N'''H^3}$	$\mathrm{O''H^2}$	$\mathrm{F'H}$
$\mathrm{Na'HO}$	$\mathrm{\cancel{Mg}''H^2O^2}$	$\mathrm{\cancel{Al}'''H^3O^3}$	$\mathrm{Si''''H^4O^4}$	$\mathrm{P^vH^3O^4}$	$\mathrm{S^{vi}H^2O^4}$	$\mathrm{Cl^{vii}HO^4}$

Having regard to the upper line of compounds, carbon may be regarded as placed at the apex of two converging series of elements of increasing atomicities; while having regard to the lower line of compounds, it will appear as the middle term of a single series. It is observable that the atomic weights of carbon and silicon correspond very closely with the arithmetical means of the atomic weights of the elements placed respectively on the same lines with them, for $\frac{88}{7} = 12{\cdot}6$ and $\frac{201}{7} = 28{\cdot}7$.

GROUP VIII. Iron Metals.—The elements previously discussed are capable of being arranged in two general divisions, accordingly as they combine with an odd or even number of atoms of halogen or hydrogen. To such of them as combine with two, four, or six atoms of chlorine, &c., the designation artiad, and to those which combine with one, three, five, or seven atoms of chlorine, &c., the designation perissad may be conveniently applied. But the metals now under consideration seem at any rate to have the property of entering into combination with chlorine, &c., in both odd and even proportions, and hence may not inappropriately receive the designation of peris-artiad. Among the members of this group attention will be more especially directed at first to the metals iron, nickel, copper, manganese, and cobalt. The most ordinary of the several series of compounds formed by these metals correspond closely with the similar compounds of zinc, in their saline constitution, water of hydration, crystalline form, and general chemical properties. Accordingly, if zinc is to be regarded as dyadic with the atomic weight 65, then iron, nickel, copper, manganese, and cobalt must also be regarded as dyadic, and receive the atomic weights given on the upper, instead of the usually received atomic weights given on the lower of the following lines:—

$\mathrm{\cancel{Fe}}$ 56	$\mathrm{\cancel{Ni}}$ 59	$\mathrm{\cancel{Cu}}$ 63·5	$\mathrm{\cancel{Mn}}$ 55	$\mathrm{\cancel{Co}}$ 59
Fe 28	Ni 29·5	Cu 31·75	Mn 27·5	Co 29·5

With these doubled atomic weights, the iron-metals will have the normal specific heat expressed approximately by the number 6·2, instead of the abnormal specific heat expressed by the number 3·1; and several other advantages resulting from the duplication will be manifested further on. Adopting, then, the atomic weights which are in harmony with the specific heats of the metals, the ordinary ferrous, manganous, &c., salts will be represented as dyad compounds by the formulæ $\text{M̶}''\mathrm{Cl}^2$, $\text{M̶}''\mathrm{O}$, $\mathrm{S}\text{M̶}''\mathrm{O}^4$, &c. Some evidence also of the existence of tetrad compounds is afforded by pyrolusite, $\text{M̶n}''''\mathrm{O}^2$, iron-pyrites, $\text{F̶e}''''\mathrm{S}^2$, and an artificial sulphide of nickel, $\text{N̶i}''''\mathrm{S}^2$. Moreover, according to experiments made by the author, there would appear to exist an unstable tetrachloride of manganese, $\text{M̶n}\mathrm{Cl}^4$, corresponding to the unstable tetrachloride of lead, $\text{P̶b}\mathrm{Cl}^4$, just as the peroxides of the two metals, $\text{M̶n}\mathrm{O}^2$ and $\text{P̶b}\mathrm{O}^2$, also correspond with one another. Be this as it may, the ferrates and manganates, $\text{F̶e}^{\text{vi}}\mathrm{K}^2\mathrm{O}^4$ and $\text{M̶n}^{\text{vi}}\mathrm{K}^2\mathrm{O}^4$, analogous to the sulphates $\mathrm{SK}^2\mathrm{O}^4$, furnish decisive examples of the existence of hexad compounds; and the mutual analogy of these three classes of salts affords an obvious argument in favour of adopting the atomic weights M̶n *55* and F̶e *56*, whereby alone they can all three be represented by analogous formulæ. The association with one another of the five metals now under consideration centres in the remarkable parallelism subsisting between nickel and cobalt. By its intermediate properties nickel serves to connect iron and copper with one another; while its relationship to the former metal corresponds evidently with that of cobalt to manganese. The association of copper with iron through the intervention of nickel seems scarcely to receive that thorough recognition to which, in the author's opinion, it is entitled (Phil. Mag. xiii. 486), apparently because of the facility with which they may be analytically separated from one another. The three metals have the same atomic volume, namely 88, which is likewise that of manganese, cobalt, and possibly chromium, but of no other metal whatever. Their specific gravities, calculated or experimental, occur in regular sequence, as do also their atomic weights. Iron is the most infusible and weldable, then nickel, then copper. The three metals are soluble in hydrochloric acid with evolution of hydrogen, iron most readily, then nickel, then copper; they precipitate the somewhat basylous metals, tin and cadmium, from their boiling solutions; and alike form salts of a marked green colour, complementary in some measure to the pink colour of manganous and cobalt salts. Their hydrates are soluble in salammoniac and ammonia, iron to a slight extent only, then nickel, copper most of all. Their sulphides are soluble in hydrochloric acid with evolution of sulphuretted hydrogen; but while the precipitation of sulphide of iron may be prevented by a slight acidulation, that of nickel requires a larger proportion, and that of copper a very much larger proportion of acid. The sulphates of iron and nickel crystallise with seven atoms of water, and are isomorphous with one another; but sulphate of copper usually crystallises with five atoms of water, and is isomorphous with the corresponding sulphate of manganese. On the other hand, the sulphates of iron and copper crystallise together in all proportions, the mixed salt being heptahydrated and having the form of sulphate of iron, or pentahydrated and having the form of sulphate of copper, according to the preponderance of either metal. Again, the double potassiosulphates of all three metals crystallise with six atoms of water, and are isomorphous. It is evident, however, in comparing the five metals with one another, that manganese and iron, which are at one extremity of the series, have a tendency to form hyperoxides, and that copper, which is at the other extremity, has a tendency to form hypo-oxides, while cobalt and nickel are intermediate both in position and tendencies. Now, it is just some of these distinctive peroxidised compounds of manganese and iron on the one hand, and suboxidised compounds of copper on the other, that furnish us with illustrations of perissad forms of combination. Thus, manganese, whose general artiad character is shown by its forming dyad, tetrad, and hexad compounds, as we have already seen, is nevertheless indisputably perissad in the permanganates. The permanganates, $\text{M̶n}^{\text{vii}}\mathrm{KO}^4$, for example, resemble the corresponding perchlorates $\mathrm{Cl}^{\text{vii}}\mathrm{KO}^4$, in constitution, stability, solubility, crystalline form, specific heat, &c., and, with the high atomic weight for manganese, are expressible by similar formulæ. The perchloric and permanganic acids are analogous, unstable, and powerfully oxidising compounds. Dumas has also described a volatile perchloride of manganese, probably a heptachloride $\text{M̶n}^{\text{vii}}\mathrm{Cl}^7$, which is decomposed by water into hydrochloric and permanganic acids.

Passing to the opposite member of the iron group we find copper furnishing a whole series of salts, which, represented by the most simple formulæ with the doubled atom of copper, C̶u *63·5*, agree closely in chemical constitution and properties, as well as in specific heat and crystalline form, with the corresponding salts of the monad metal silver. Cuprous chloride $\text{C̶u}\mathrm{Cl}$, and silver chloride AgCl, agree in the following characters. They have the same specific heat and crystalline form; are producible as white precipitates insoluble in water, but soluble in ammonia and in boiling hydrochloric acid, to form colourless solutions. They dissolve also in solutions of the alkaline chlorides forming similar double salts, which Becquerel obtained electrolytically in crystalline forms belonging to the regular system. The bromides and iodides of both metals correspond with one another and with the chlorides, in form, solubility, reaction with ammonia, production of double salts, &c. &c. The amorphous oxides, Cu^2O and Ag^2O, resemble one another, but oxide of copper has alone been obtained in crystals, which are octahedral. The sulphides exhibit a remarkable correlation. Cuprous sulphide, Cu^2S, is dimorphous, and while the artificial compound is isomorphous with silver-glance, Ag^2S, in the regular system, the native form or copper-glance is isomorphous with silver-copper-glance, $AgCuS$, in the trimetric system. Miargyrite and antimonial copper are similarly constituted compounds, $AgSbS^2$ and $CuSbS^2$ respectively, while bournonite $Pb''CuSbS^3$, and red silver Ag^3SbS^3, are similar and isomorphous. The convertibility of cuprous into cupric compounds constitutes, indeed, the only marked peculiarity of behaviour distinguishing them from the similar compounds of silver. So long as they continue to be cuprous compounds, the resemblance between them and their silver analogues is as great as that between the corresponding compounds of any two associated metals. But despite the analogy of cuprous to silver chloride, for instance, and of permanganic to perchloric acid, it has been proposed to double the molecular formulæ of all cuprous and permanganic compounds, and consequently to express them by formulæ dissimilar to those of their respective silver and chlorine analogues. By this means the formulæ Cu^2Cl^2 and $Mn^2H^2O^8$, for instance, will certainly be brought into harmony with the law of even numbers, but at a very heavy sacrifice of simplicity and analogy. Fully admitting the great and not generally appreciated value of Laurent and Gerhardt's law, it must yet be remembered that these distinguished chemists themselves pointed out its inapplicability to the perissad compounds of the iron metals, save by admitting for each metal two different atoms represented by two different symbols; and it may also be asked whether the received mode of expressing Laurent and Gerhardt's law might not be advantageously modified into some such dictum as the following, that "in every compound the sum of the atomicities or equivalencies is an even number."

Just as copper and manganese, though usually dyadic, are associated with monadic silver and heptadic chlorine respectively, so is iron, though usually dyadic, associated with triadic aluminium. Ferric chloride, oxide, and compounds generally, present such an analogy to aluminic chloride, oxide, and compounds generally, that similar formulæ ought necessarily to be applied to the similar series of bodies. Confining ourselves for simplicity's sake to the case of the two chlorides, we have to choose between the formulæ $AlCl^3$ and $FeCl^3$, on the one hand, and the formulæ Al^2Cl^6 and Fe^2Cl^6, on the other. The more complex expression for ferric-chloride, Fe^2Cl^6, is certainly recommended by several considerations of indisputable importance, but not, in the author's opinion, of such paramount importance as positively to require its adoption. Thus, the formula Fe^2Cl^6 is in harmony with the law of even numbers, as usually enunciated; but the simpler formula would agree equally well with the law, if modified in its expression as above proposed. Again, the formula Fe^2Cl^6 is in harmony with the constitution of certain mixed and basic salts of ferricum investigated more particularly by Scheurer-Kestner (Bull. Soc. Chim. 1863, p. 344), in which one-sixth of the acid radicle combined with the ferricum differs from the remaining five-sixths, as in ferric aceto-nitrate, for example, $Fe^2(C^2H^3O^2)^3(NO^3)^2HO$, or $Fe(C^2H^3O^2)^3.Fe(NO^3)^2HO$; but the number of salts known to be formed on duplicate types is now so great as to deprive this consideration of any extreme consequence. No one, for instance, contends that the constitution of tri-acid oxalate of potassium, $C^2H^2O^4.C^2HKO^4$, necessitates the accordance of the formula $C^4H^4O^8$ to oxalic acid. Lastly, the formula Fe^2Cl^6 is in harmony with the vapour-density of ferric chloride, as determined by Deville, who found that two volumes of vaporised ferric chloride contain twice 56 parts of iron, and six times 35·5 parts of chlorine, just as two volumes of vaporised chloride of aluminium contain twice 27·5 parts of aluminium, and six times 35·5 parts of chlorine. This is no doubt a very important result, and one which, unless susceptible of some explanation direct or analogical, would be decisive of the question. But there are undoubtedly certain bodies of which the ascertained vapour-densities, no matter how accounted for, are, as a matter of experiment, discordant with the chemical analogies of the respective bodies. For instance, the quantity of phosphorus which bears to the molecule of phosphoretted hydrogen, PH^3, the same relation that the molecule of nitrogen bears to the molecule of ammonia, has only half the bulk of these several molecules. Again, the quantity of white arsenic which bears to the molecule of arsenious chloride, $AsCl^3$, the same relation that the molecule of water bears to the molecule of hydrochloric acid, has only half the bulk of these several molecules. Lastly, the quantity of aluminic chloride which bears to the molecule of aluminic ethide, $AlEt^3$, the relation which the molecule of corrosive sublimate bears to the molecule of mercuric ethide, has only half the bulk of these several molecules. In these cases, the results flowing from the anomalous volumes of free phosphorus, arsenious oxide, and aluminic chloride are corrected by having regard to the normal volumes of other volatile compounds of phosphorus, arsenic, and aluminium respectively; and bearing in mind the great resemblance between aluminic and ferric compounds, is it not probable that the ascertained volume of ferric chloride may be also anomalous, and hereafter be proved to be anomalous by comparison with the vapour-densities of as yet undiscovered volatile compounds of ferricum having normal volumes? Whether it be that certain bodies have two distinct condensations corresponding to two distinct molecules, of which in some cases the ordinary, in some cases the extraordinary, and in other cases both, are experimentally known; or whether it be that these bodies have each in reality but a single condensation and a single molecule, which in some cases has not been correctly ascertained through the employment of a temperature insufficient to render the body perfectly elastic, the fact remains that the ascertained vapour-densities of a considerable number of bodies are not in harmony with their most characteristic chemical relations, though, in the majority of instances, these anomalous results are divested of importance by other determinations of vapour-density, either of the same bodies raised to higher temperatures, or of allied bodies having a more decided volatility. Even allowing, therefore, that ferric chloride, at the temperature at which its density was taken, has the molecular formula $\mathrm{Fe^2Cl^6}$, it by no means follows that under other conditions it may not have the simpler molecular formula $\mathrm{FeCl^3}$. Admitting the probable existence of a tetrachloride of iron, $\mathrm{FeCl^4}$, as suggested by Friedel (Wurtz, Leçons de Philosophie Chimique, 160), and by Erlenmeyer (Zeitschr. Chem. Pharm. 1862, p. 129), there may really be a $\frac{3}{2}$-chloride formed by the union of two atoms of this tetrachloride with elimination of a molecule of chlorine, or what comes to the same thing, by the union of an atom of tetrachloride with an atom of dichloride of iron into an intermediate compound; but the general habitudes of ordinary ferric chloride scarcely correspond with its possession of such a composite character. On the contrary, we find ferricum persistent as such through an entire series of salts, which under no circumstances behave like diameric compounds by breaking up into their di- and tetra- progenitors. And if ferric chloride, $\mathrm{Fe^2Cl^6}$, for instance, be not diameric, its production from ferrous chloride becomes quite inexplicable. For it is scarcely conceivable, and certainly contrary to all analogy, that the first action of chlorine upon iron should be to produce a dichloride $\mathrm{FeCl^2}$, and that its continued action should have the effect of uniting two molecules of this chloride into one single molecule of a non-diameric higher chloride according to the equation $\mathrm{2FeCl^2 + Cl^2 = Fe^2Cl^6}$: for the action of chlorine and oxygenants in general is habitually to effect the breaking up, never the building up of complex molecules, save of such as are decidedly diameric. Accepting the formula $\mathrm{FeCl^3}$ for the chloride, certain other important ferric compounds will be represented as follows: the hydrates as $\mathrm{Fe'''H^3O^3}$ and $\mathrm{Fe'''HO^2}$; the oxide as $\mathrm{Fe^{\prime\prime\prime 2}O^3}$; the black oxide as $\mathrm{FeOFe^{\prime\prime\prime 2}O^3}$ or $\mathrm{Fe^3O^4}$; and iron alum as $\mathrm{KFe'''(SO^4)^2.12H^2O}$. Thus the constitution of iron alum, like that of common alum, becomes a direct consequence of the triatomicity of its characteristic metal. Cobalt and manganese both form oxides corresponding to ferric oxide, and manganese forms in addition an unstable manganic chloride, $\mathrm{Mn'''Cl^3}$, and manganic alum, $\mathrm{KMn'''(SO^4)^2.12H^2O}$. These formulæ of course depend for their warranty upon those for the corresponding ferric compounds. It is observable that of the entire series of perissad chlorides, $\mathrm{M'Cl}$, $\mathrm{M'''Cl^3}$, $\mathrm{M^{v}Cl^5}$, and $\mathrm{M^{vii}Cl^7}$, the pentachloride is alone unrepresented in the iron family of elements.

Chromium serves to connect the iron metals with vanadium. According to it the normal atomic heat 6·2, its atomic weight will be 52·5, instead of 26·25, the heretofore generally received number. It forms three well-defined chlorides, viz. the dichloride $\mathrm{Cr''Cl^2}$, trichloride $\mathrm{Cr'''Cl^3}$, and oxychloride or chlorochromic acid $\mathrm{Cr^{vi}Cl^2O^2}$. This last compound is readily volatile, and its ascertained vapour-density being the half of its atomic weight, its molecule is referrible to the normal two-volume standard. The dichloride and trichloride are also volatilisable compounds, but their vapour-densities have not been determined. That of the trichloride, however, would probably present the same peculiarity as the analogous aluminic and ferric trichlorides; and judging solely by vapour-density, the compound would consequently have to be represented by the formula $\mathrm{Cr^2Cl^6}$ Chromous salts correspond closely to ferrous salts in their general behaviour, and especially in their absorption of nitric oxide, with production of dark brown compounds. They have, however, a red or bluish colour more like that of cobalt salts. Alkaline sulphydrates throw down a black precipitate of chromous sulphide, and caustic alkalis a pale coloured precipitate of chromous hydrate, soluble in salammoniac and ammonia. The tendency of this last precipitate to become peroxidised greatly exceeds even that of ferrous hydrate, as proved by its gradual deoxidation of water with liberation of hydrogen. The double sulphate of chrome and potassium, $\mathrm{K^2Cr''(SO^4)^26H^2O}$, is isomorphous with the similar salts of iron, &c. Chromic and ferric compounds again present a general similarity of behaviour, though with some well-marked differences. Chrome-iron $\mathrm{Fe''Cr^{\prime\prime\prime 2}O^4}$ is isomorphous with magnetic oxide $\mathrm{Fe''Fe^{\prime\prime\prime 2}O^4}$;

chromic oxide $\text{Ȼr}'''^{2}O^{3}$, with hæmatite $Fe'''^{2}O^{3}$; chromic alum $K\text{Ȼr}'''(SO^{4})^{2}.12H^{2}O$, with iron alum $KFe'''(SO^{4})^{2}.12H^{2}O$, &c. But, unlike the similar compounds of ferricum, chromic oxide is decomposed by fusion with carbonated alkalis into chromate and an inferior oxide; chromic hydrate is soluble in cold solutions of caustic alkalis; while chromic salts react with sulphide of ammonium to produce chromic hydrate and sulphuretted hydrogen, though this last difference may possibly be only one of degree depending upon the difficult reducibility of chromic compounds: for it is doubtful at least whether the precipitate produced by sulphide of ammonium in ferric salts is other than a mixture of sulphur and ferrous sulphide. However, chromic anhydride $\text{Ȼr}O^{3}$, the most characteristic of all the compounds of chrome, though forming salts having the same general formula as the manganates and ferrates $XM^{2}O^{4}$, seems in other respects to have no affinity with compounds of the iron class of metals, while it is associated with vanadic anhydride $\text{Ꝟ}O^{3}$, by many very marked similarities. The two oxides are orange-coloured, non-volatile, fusible, crystalline solids, soluble in water and decomposible by heat, that of chromium by far the most readily. They neither of them form definite hydrates or acids, but unite with basic oxides to form very stable salts of an orange colour, such as the native chromate of lead $\text{ȻrⱣb}O^{4}$, and vanadate of lead $\text{ꝞⱣb}O^{4}$, which are isomorphous, and the very characteristic anhydro-bichromate $\text{Ȼr}^{2}K^{2}O^{7}$, and anhydro-bivanadate of potassium $\text{Ꝟ}^{2}K^{2}O^{7}$. Again, both anhydrides act as feeble bases to the stronger acids, that of vanadium, however, to considerably the greatest extent. The aqueous solutions of the two compounds are reduced by the same reagents, and appear to react in a similar manner with peroxide of hydrogen. The hexachloride of vanadium $\text{Ꝟ}Cl^{6}$, corresponding to the anhydride and to chlorochromic acid $\text{Ȼr}^{2}Cl^{2}O''$, seems to undergo when vaporised a dissociation similar to that of pentachloride of phosphorus, PCl^{5}; at any rate its vapour-density is only one-fourth its recognised molecular weight, which accordingly corresponds to four volumes. The tendency of vanadium to form sulphides having the character of sulphanhydrides, though not very decided, has no parallel in the known behaviour of chromium; while the inferior oxides and saline compounds of the two metals certainly present very little co-resemblance, unless indeed the blue salts of vanadium, produced by reduction of vanadic anhydride, should prove to be trisalts (sesquisalts), analogous to the ordinary green chromic salts produced under similar circumstances. The atomic heat of vanadium has not been ascertained, but the proportion of the metal which corresponds with 52·5 parts of chromium in the respective trioxides, is found to be 137 parts, and accordingly the atomic weight of vanadium is fixed at 137, instead of 68·5 as previously. It is observable that the difference between the atomic weights of chromium and vanadium, or 94·5, is about the same as that subsisting between the atomic weights of the first and last members of several triplet groups of elements. Moreover, the atomic weight of vanadium is almost the arithmetic mean of the atomic weights of molybdenum and tungsten, elements with which vanadium is not unfrequently classified, and to which it certainly presents some analogy, more particularly in the character of its inferior compounds.

Uranium is usually classed with the iron metals, for although possessing but little resemblance even to them, it has still less to any other group of elements. The formulæ of uranium-compounds, and the atomic weight of uranium must be regarded for the present as undeterminable, since the analytical results cannot yet be controlled by any considerations derived from vapour-density, isomorphism, specific heat, or strict chemical analogy. The proportion of uranium which unites with 35·5 parts of chlorine in uranous chloride, is found to be 60 parts, and accordingly the atomic weight of the metal may be fixed at 60, or 120, or 180, &c. The ready volatility of uranous chloride is in favour of its molecule containing more than one, and indeed even more than two atoms of chlorine; while the high specific gravity of uranium, 18·4, would seem to associate its atomic weight with those of such heavy metals as tungsten, specific gravity 17·6, atomic weight 184; gold, specific gravity 19·3, atomic weight 196·5; and platinum, specific gravity 21·5, atomic weight 197; although the correlation of specific gravity with atomic weight is undoubtedly subject to many vagaries. Altogether, however, in the present imperfect state of knowledge, it seems most advisable to assume that the atomic weight of uranium is 120, and that the formula of its subchloride is $\text{Ʉ}^{2}Cl^{3}$, while that of uranous chloride is $\text{Ʉ}''Cl^{2}$, and that of uranic oxychloride $\text{Ʉ}'''O''Cl$. Aqueous uranous chloride and uranous salts in general have a marked green colour, but furnish a red-brown gelatinous hydrate, soluble in carbonated alkalis. Unlike the majority of dyad salts, they are completely decomposed by the earthy carbonates, with evolution of carbonic anhydride. They yield a black precipitate with sulphide of ammonium, and oxidise readily by exposure to air. Uranic salts are of a lemon-yellow colour, and possess in a characteristic degree the property faintly shadowed forth in a few trisalts of antimony, chromium, &c., of being derived from their respective acids by a substitution, not of metal, but of metallic oxide for basic hydrogen, which metallic oxide is transferable from one compound to another, throughout the entire series of double decompositions to which the salts are liable. There is accordingly no trichloride UCl^3 or trinitrate $U(NO^3)^3$, but only an oxychloride $UO''Cl$ and oxynitrate $UO''NO^3$. The oxychloride is a yellow crystalline, readily fusible but difficultly volatilisable mass. The nitrate crystallises in lemon-yellow prisms decomposible by heat, and yielding in succession a uranic hydrate, uranic oxide, and uranoso-uranic oxide. Both salts are soluble in water, forming lemon-yellow fluorescent solutions. These are converted into uranous solutions by sulphuretted hydrogen, with separation of sulphur, and are otherwise very easily reducible. They give a dark brown precipitate with sulphide of ammonium; form soluble crystallisable double compounds with excess of alkaline carbonate, the potassium-salt having the formula $2K^2CO^3.(UO)^2CO^3$; and yield precipitates of alkaline uranite, $K^2O.2U^2O^3$, for instance, with caustic alkalis.

Group IX. **Platinum Metals.**—The metals **palladium**, **rhodium**, **ruthenium**, **platinum**, **iridium**, and **osmium**, though differing considerably in many of their chemical habitudes, are nevertheless separated from all other elements, and associated with one another, by certain very distinctive characters. With the normal atomic heat 6·2, their several atomic weights will be as follows:—Os 199, Ir 197, Pt 197, Pd 106·5, Ru 104, and Rh 104. The specific gravities of the first three metals having the higher atomic weights are about 21, while those of the other three having the lower atomic weights are between 11½ and 12. Each of the metals of low atomic weight seems to be more especially correlated with some particular one of the metals of high atomic weight, palladium with platinum, rhodium with iridium, and ruthenium with osmium; and all six metals are found associated together naturally in the metallic state. They are all infusible save at the highest temperatures, such as that attainable with the oxyhydrogen blowpipe. The platinum metals resemble certain metals of the iron family in the polychromatism of their salts, the permanency of their double cyanides, and the perissartiad seriation of their chlorides, oxides, &c.

Palladium and platinum belong to the class of noble metals. They do not combine directly with oxygen, even at the highest temperatures, while their chlorides and indirectly produced oxides are reducible to the reguline state by heat alone. Their di- and tetrachlorides are the most characteristic of their combinations. Palladium is said to form an inferior chloride $PdCl$, and oxide Pd^2O, analogous to those of cuprosum, but its ordinary salts are typified, as above remarked, by the dichloride $PdCl^2$, and the tetrachloride $PdCl^4$. The former is crystallisable and soluble in water, while the latter is known only in solution. They both produce crystallisable double salts with chloride of potassium, ammonium, &c. Platinum forms a well-defined crystalline tetrachloride $PtCl^4$, which by a regulated heat is convertible into the dichloride $PtCl^2$, insoluble in water but soluble in hydrochloric acid, and also in solution of the tetrachloride, forming apparently a double or intermediate chloride Pt^2Cl^6 or $PtCl^3$. Both the di- and tetrachlorides of platinum form crystallisable double salts with the chlorides of alkali-metal, &c.

Rhodium and iridium, though permanent in the air at all temperatures when in the massive state, seem to be more readily oxidisable by treatment with chemical agents than the metals last considered. At the same time their several oxides are reducible by heat alone. The trichlorides are the most characteristic of their respective chlorides, and are typical of their ordinary salts. Rhodium forms an insoluble dichloride $RhCl^2$ of which very little is known, and a soluble deliquescent rose-coloured trichloride $RhCl^3$, one atom of which combines with either two or three atoms of alkaline chloride to form beautiful crystalline salts of a rose-red colour, whence the name of the metal. Iridium, so called from the polychromatism of its salts, forms a dichloride $IrCl^2$, insoluble in water, but forming soluble red coloured salts with the alkaline chlorides; a comparatively stable trichloride $IrCl^3$, whose solution is of an olive-green colour, and whose double potassio-chloride has the formula $3KCl.IrCl^3$; and a tetrachloride $IrCl^4$, known only in the form of its potassio-chloride $2KCl.IrCl^4$, which is a crystallisable salt of almost black colour, while the corresponding hydrated oxide $IrO^2.2H^2O$, occurs as an indigo-blue precipitate.

Ruthenium and osmium differ from the other platinum-metals in the degree of their oxidisability, ruthenium forming a trioxide RuO^3, corresponding to an unknown hexachloride $RuCl^6$, and osmium forming both a trioxide OsO^3, with its corresponding chloride $OsCl^6$, and a stable volatile tetroxide OsO^4, the most highly oxidised compound of any element whatsoever. Ruthenium and osmium, moreover, are directly oxidisable, and even combustible, in air, at temperatures varying with their state of aggregation, and the resulting oxides are not reducible by any increased temperature to which they have been subjected. Ruthenium forms three chlorides $RuCl^2$, $RuCl^3$, and $RuCl^4$, with the corresponding oxides RuO, Ru^2O^3, and RuO^2, of which the trichloride and trioxide are typical of ordinary ruthenium salts. The dioxide, produced by heating ruthenium with osmium in a current of air, though not volatile *per se*, is carried over by the osmic vapours and condenses as a crystalline sublimate of well-defined square prisms. Fused with nitre, all the above oxides of ruthenium produce a soluble orange-yellow salt, the rutheniate of potassium $K^2O.RuO^3$. Osmium forms four chlorides $OsCl^2$, $OsCl^3$, $OsCl^4$, and $OsCl^6$, all of which volatilise by heat and produce double salts with the alkaline chlorides. It also forms the corresponding oxides OsO, Os^2O^3, OsO^2, OsO^3, and an additional oxide OsO^4. The trioxide, though scarcely known, save in the form of its potassium-salt $K^2O.OsO^3.2H^2O$, which crystallises in rose-coloured octahedra, seems to have decided acid characters. Tetroxide of osmium OsO^4 is a very remarkable body. It occurs in flexible acicular colourless crystals, freely soluble in water. It fuses at a gentle heat and boils at 100°, with conversion into a pungent noxious vapour, whose specific gravity is the half of its atomic weight. It seems to be quite devoid of acid properties, since it is evolved from its solution in caustic alkalis by simple ebullition, while its solution in water has no action upon litmus paper.

The numerical relations subsisting between the atomic weights of the several elements have for a long time past excited considerable interest among chemists, and have not unnaturally led to a considerable amount of speculation. Dumas, at the meeting of the British Association in 1851, first directed prominent attention to the subject, and some years afterwards published a detailed account of his conclusions thereon (Ann. Ch. Phys. [3] lv. 129), of which the following statement with regard to the halogen elements may be taken as an illustration. Calling the equivalent of fluorine *a*, the difference between that and the equivalent of chlorine *d*, and a complementary difference which is required in order to pass from chlorine to bromine, *d'*, there is obtained, for fluorine, chlorine, bromine, and iodine, the series—

$$\begin{array}{rlrl}
a & \text{or} & 19 \quad . \quad . \quad . \quad . \quad . & = 19 \\
a + d & „ & 19 + 16{\cdot}5 \quad . \quad . \quad . \quad . & = 35{\cdot}5 \\
a + 2d + d' & „ & 19 + 33 + 28 \quad . \quad . \quad . & = 80 \\
2a + 2d + 2d' & „ & 38 + 33 + 56 \quad . \quad . \quad . & = 127
\end{array}$$

It may suffice, however, to remark in this place that very many of the elements seem to be associated in groups formed of three terms, and that the difference in atomic weight between any two proximate terms is always very nearly 40, or 44, or 48; and, consequently, that the difference between the first and third terms is nearly 84, or 88. or 92, or 96. Moreover, to several of these groups of three, there is appended a fourth term, in which case the difference in atomic weight between the third and fourth terms is the same as that between the first and third terms, namely 88, and in one instance 92. Lastly, to several of the groups of three or four, there is prefixed an initial term, in which case the difference in atomic weight between the initial term and the first of the remaining terms is approximately 16. Allowing chromium and manganese to stand proxy for the iron metals, and palladium and platinum for their respective congeners, the following table, slightly modified from one published by the author a few months back (Quart. Journ. of Science, i. 643) contains a list of all the well-known elements arranged horizontally in the order of their generally received groups, and perpendicularly in the order of their several atomic weights.

			Mo 96	W 184
			—	Au 196·5
			Pd 106·5	Pt 197
L 7	Na 23	—	Ag 108	—
G 9	Mg 24	Zn 65	Cd 112	Hg 200
B 11	Al 27·5	—	—	Tl 203
C 12	Si 28	—	Sn 118	Pb 207
N 14	P 31	As 75	Sb 122	Bi 210
O 16	S 32	Se 79·5	Te 129	—
F 19	Cl 35·5	Br 80	I 127	—
	K 39	Rb 85	Cs 133	—
	Ca 40	Sr 87·5	Ba 137	—
	Ti 48	Zr 89·5	—	Th 231
	Cr 52·5	—	V 138	—
	Mn 55 &c.			

It is observable that the difference in atomic weight of 16 subsists, not only between the elements of the first and those of the second column, but also between sodium and potassium, magnesium and calcium, and selenium and molybdenum respectively; while a difference of about 20 subsists between the atomic weights of silicon and titanium, sulphur and chromium, and chlorine and manganese respectively. Many other relations of interest are also evident upon simple inspection; and it may, perhaps, be worthy of note that, where the difference in atomic weight between proximate elements is about 48, the resemblance in properties is usually more decided than where the difference is 44 or 40. Doubtless some of the arithmetical relations exemplified in the foregoing table are merely accidental, but, taken altogether, they are too numerous and decided not to depend upon some hitherto unrecognised general law. W. O.

METALUMINA. This name is applied by Graham (Chem. Soc. J. xv. 24) to the soluble dihydrate of aluminium (i. 159) which Crum obtained by the action of heat on a solution of the acetate. Graham has shown that it may be prepared by dialysing a solution of the acetate altered by heat, nearly all the acetic acid passing through, and a solution of metalumina remaining on the dialyser (p. 717). The solution is tasteless, and neutral to test-paper.

METALYSIS. Döbereiner's name for CATALYSIS.

METAMARGARIC ACID. An acid isomeric with margaric acid, $C^{17}H^{34}O^2$, said by Frémy (Ann. Ch. Phys. [2] lxv. 121) to be obtained, together with meta-oleic acid, by treating with cold water the mixture of sulphomargaric and sulpholeic acids produced by the action of strong sulphuric acid upon olive-oil. On pressing the resulting precipitate, and treating it with alcohol of 36 per cent., the metamargaric acid is dissolved out. It is white, crystalline, insoluble in water, easily soluble in alcohol and ether, melts at 50°, and exhibits the composition of margaric acid. Most of its salts were also found by Frémy to exhibit the composition of the margarates, but the silver salt yielded 27—85 per cent. silver, which is nearly the composition of stearate of silver. Altogether, it is doubtful whether the acid obtained as above was a definite compound.

METAMERISM. See ISOMERISM (p. 415).

METAMECONIC ACID. Syn. with COMENIC ACID (i. 1103).

METAMORPHINE. An opium-base, the hydrochlorate of which is obtained, as a residue, in the preparation of opium-tincture by means of lime and sal-ammoniac. The *hydrochlorate* is soluble in 25 pts. of cold, and 2 pts. of hot water, reacts neutral, and gives no precipitate, either with ammonia or with the fixed alkalis or their carbonates. When dried at 100°, it contains 12·2 per cent. HCl (hydrochlorate of morphine, $C^{17}H^{19}NO^3.HCl.3H^2O$, contains 9·7 per cent.).

The free base separated from the sulphate by digestion with carbonate of barium, and exhaustion with alcohol, crystallises in stellate groups of prisms. It is not bitter; dissolves in 600 pts. cold, and 70 pts. boiling water, in 330 pts. of alcohol of 90 per cent. at ordinary temperatures, and in 9 pts. at the boiling heat; it is nearly insoluble in ether. It dissolves easily in caustic potash, less easily in ammonia and alkaline carbonates. With nitric acid of specific gravity 1·33 it forms a yellow solution. The aqueous solution is gradually coloured yellow by iodic acid; not altered by ferric chloride. Chloride of gold first forms with it a yellowish colour, then a flocculent brownish precipitate, but produces no blue coloration. (G. C. Wittstein, Arch. Pharm. [2] cv. 141.)

METAMORPHISM. A term applied to the transformation of minerals and rocks by physical and chemical action. (See GEOLOGY, CHEMISTRY OF, ii. 831.)

METAMYLENE. A compound polymeric with amylene, probably $C^{20}H^{40}$, contained in the higher portion of the distillate produced by heating amylic alcohol with sulphuric acid. It has not been obtained pure. (Balard.)

METANAPHTHALENE. See NAPHTHALENE.

METANTIMONIC ACID. See ANTIMONY (i. 324).

META-OCTYLENE. See OCTYLENE.

META-OLEIC ACID. An oily acid produced by the action of water on sulpholeic acid. It is insoluble in water, easily soluble in ether, very slightly in alcohol. (Frémy, Ann. Ch. Phys. [2] xv. 128.)

METAPECTIC ACID. See PECTIC ACID.

METAPECTIN. See PECTIN.

METAPHOSPHORIC ACID. See PHOSPHORUS, OXYGEN-ACIDS OF.

METASILICATES. Silicates of the augite type, M^2SiO^3 or $M^2O.SiO^2$ (Odling.)

METASTANNIC ACID. See Stannic Acid, under Tin.

METASTYROL. Syn. with Metacinnamene (see Cinnamene, i. 982).

METATARTARIC ACID. See Tartaric Acid.

METATEREBENTHENE. See Turpentine.

METATUNGSTIC ACID. See Tungstic Acid.

METAXITE. Breithaupt's name for a fibrous variety of serpentine from Schwarzenberg in Saxony. Hardness = 2 to 2·5. Specific gravity = 2·52. Greenish-white, with weak pearly lustre. Contains, according to Kühn (Ann. Ch. Pharm. lix. 369), 43·48 per cent. silica, 41·00 magnesia, 2·20 ferrous oxide, and 12·95 water (= 99·63).

METAXOÏTE. A mineral resembling metaxite, occurring in green serpentine at Lupikko, near Pitkåranta in Finland. Hardness, between calcspar and gypsum. Specific gravity = 2·58 to 2·61. Colour, from greenish-black to white. Sometimes apparently amorphous, sometimes radio-fibrous and spherical. Contains, according to an analysis by C. G. Hällsten (Jahresb. 1862, p. 749), 40·63 per cent. silica, 10·17 alumina, 6·78 ferric oxide, 12·88 magnesia, 16·03 lime, and 12·88 water (= 99·37).

METEORIC DUST.
METEORIC IRON.
METEORIC MUD.
METEORIC STONES.
} See the next article.

METEORITES. *Aerolites. Uranolites.* This name includes, not only those mineral bodies which are known to have fallen on the earth's surface from the celestial spaces, but likewise a great number of others, which, though their origin is not actually known, yet agree so closely with known meteorites in mineralogical and chemical constitution, as to justify the conclusion that they are also of meteoric origin.

The numerous analyses which have been made of meteorites, both the older ones by Howard, Klaproth, and Vauquelin, and those of more recent date by Berzelius and others, have demonstrated in them the presence of about 18 elementary bodies, all of which likewise occur in terrestrial minerals, viz. aluminium, calcium, carbon, chromium, cobalt, copper, iron, magnesium, manganese, nickel, oxygen, phosphorus, potassium, silicium, sulphur, titanium, tin, and perhaps also in some cases, antimony, arsenic, chlorine, hydrogen and lead.

Meteorites are divided into two classes, distinguished as Meteoric Iron, and Meteoric Stones. Meteoric iron consists chiefly of metallic iron alloyed with nickel, contains no oxidised compound, and has in general the characters of ordinary bar-iron. Meteoric stones are mixtures of several minerals, chiefly silicates (felspar, augite, olivin), which also play an important part in terrestrial minerals.

This division is however merely artificial, inasmuch as many meteorites are mixtures of meteoric iron with masses of meteoric stone, or with one or more of the minerals occurring in meteoric stones. If the metallic portion predominates, the meteorite is classed as meteoric iron, as for example the so-called Pallas meteorite, found at Krasnojarsk in Siberia, or that of Atacama, both of which contain larger or smaller masses of olivin imbedded in cavities in the iron. If, on the other hand, the earthy portion (the silicates) predominates in amount, the meteorite is called a meteoric stone, although the fine splinters or grains of meteoric iron diffused through the mass may give it an appearance quite different from that of meteoric stones consisting wholly of earthy minerals. Meteoric stones containing metallic iron are much more numerous than those consisting wholly of earthy minerals.

1. Meteoric Iron.

A mass of meteoric iron is always a mixture, the constituents being sometimes visible, sometimes revealing themselves only to chemical investigation. The chief part of the mass consists of iron alloyed with nickel, and perhaps always with a small quantity of cobalt. This admixture of nickel is usually regarded as a proof of the meteoric origin of numerous masses of metallic iron found on or a little below the surface of the earth, whose actual fall has not been observed. The amount of iron in meteoric iron usually varies from about 80 to 95 per cent.; the nickel from 6 to 10 per cent.

In many cases, sulphide of iron is visibly disseminated through the mass, sometimes in the form of rather large cylindrical grains. This sulphide is often regarded as magnetic pyrites, Fe^3S^2 (p. 401), which does indeed occur in some meteorites; but those examined by Rammelsberg (Pogg. Ann. cxxi. 363) contained protosulphide of iron, Fe^2S. Part of this sulphide is however distributed through the mass of the iron in so minute a state of division, that it can be detected only by the evolution of sulphydric acid, which takes place on dissolving the iron in acids.

Moreover all specimens of meteoric iron, when dissolved in hydrochloric acid, leave a residue, varying in amount from a fraction to several units per cent. This residue is also a mixture, and appears under the microscope to consist chiefly of a distinctly crystallised compound, which chemical analysis shows to contain iron, nickel, and phosphorus, usually mixed with carbon and silica. The carbon, a very remarkable constituent of meteoric iron, appears to occur therein, as in pig-iron, in two different states, viz. partly as graphite, partly in chemical combination with the iron. On this account, the entire quantity of the carbon is never found in the residue, the solution of meteoric iron in acids being attended with the emission of the same offensive odour that is evolved in the solution of pig-iron. The silica is derived from silicide of iron. It is evident from these considerations that chemical analysis can never afford a perfectly exact picture of the individual compounds present in meteoric iron.

Many specimens of meteoric iron, when polished and afterwards etched with an acid, exhibit on their surface peculiar crystalline configurations, called 'Widmanstädt's figures.' These figures were attributed by Berzelius to an alloy of iron and nickel disseminated through the mass, which alloy, being less soluble in acids than the pure iron, was brought to light when the latter was removed from the surface by the acid. But certain samples of meteoric iron, viz. that of the Cape (p. 379), and those found at Greenville in Tennessee and at Clairborne in Alabama, all very rich in nickel (containing from 9 to 12 per cent. of that metal), do not exhibit these figures: hence their formation is much more probably due to the phosphide of nickel and iron, or *Schreibersite* (Shepard's *Dyslytite*), which, as already observed, forms the principal part of the residue left on dissolving the iron in acids.

The analysis of the principal mass of the iron often exhibits small quantities of phosphorus, doubtless arising from partial decomposition of the phosphide by the acid used to dissolve the iron.

The following are analyses of a few specimens of meteoric iron, taken from Rammelsberg's *Mineralchemie* (pp. 902-920).

1. Found at Elbogen in Bohemia, and known as 'der verwünschte Berggraf.' Specific gravity, as determined by different observers, 7·74—7·83. In the solution of this meteorite in hydrochloric acid, Berzelius found traces of tin and copper. The residue is a mass having a carbonaceous aspect, and consisting partly of metallic spangles.

2. Bohumilitz in Bohemia. Specific gravity = 7·14 (Steinmann); 7·61—7·71 (Rumler). Dissolves in hydrochloric acid, with evolution of fetid hydrogen gas; the solution contains traces of phosphorus.

3. Seeläsgen near Schwiebus. Specific gravity = 7·59 (Partsch); 7·63—7·1, (Duflos); 7·7345 (Rammelsberg). In the metallic mass are enclosed cylindrical grains of a sulphide of iron, of brownish-yellow colour, specific gravity 4·787, quite insoluble in hydrochloric acid, and containing, according to Rammelsberg's analysis, 75·37 per cent. ferrous sulphide, 0·71 sulphide of copper, 2·73 chrome-iron, and 19·83 nickel-iron (= 98·64).

4. Krasnojarsk in Siberia. Discovered in 1772 by Pallas, and hence called the Pallas mass. The best known meteorite of the class, consisting of metallic nickel-iron mixed with olivin and a little sulphide of iron. Specific gravity = 7·78—7·84 (Rumler). The residue insoluble in hydrochloric acid contains, besides charcoal, a heavy substance having the metallic lustre and appearing distinctly crystalline under the microscope.

5. Cosby's Creek, Cooke County, Tennessee. Specific gravity = 7·26 (Rumler); 7·257 (Bergemann). The residue, according to Bergemann, is a black powder amounting to 2·075 per cent., containing yellow shining magnetic laminæ and a black coaly mass.

6. Braunau in Bohemia. Fell on July 14, 1847. Specific gravity = 7·714 (Beinert). The insoluble residue is a mixture of an amorphous coaly powder, with greyish-white, metallic-shining, strongly magnetic laminæ. In the mass is imbedded a magnetic sulphide of iron, which dissolves in hydrochloric acid without separation of sulphur, but leaves very small quantities of charcoal and chrome-iron.

7. Coahuila in Mexico. A mass weighing 252 pounds. Specific gravity = 7·81. The phosphide is said to amount to 1·55 per cent.

8. Atacama in Chile. Specific gravity = 7·89. The cavities contain a brownish-white silicate of calcium and iron, containing phosphoric acid (perhaps olivin).

9. Niakornak in Greenland. Specific gravity = 7·073. When dissolved it gives off hydrogen gas containing sulphur and carbon, and leaves at first a crystalline

Analyses of Meteoric Iron.

		1.	2.	3.	4.	5.	6.
Analyst.		Berzelius.	Berzelius.	Rammelsberg.	Berzelius.	Bergemann.	Duflos a. Fischer.
Iron		88·23	93·77	92·33	88·04	90·09	91·88
Nickel		8·52	3·81	6·23	10·73	6·52	5·52
Cobalt		0·76	0·21	0·67	0·46	0·33	0·53
Manganese		. .	. .	. .	0·13	. .	0·77†
Copper		. .	. .	0·05	0·07	. .	
Magnesium		0·28	. .	. .	0·05	. .	
Silicium		. .	. .	0·02	.	. .	
Carbon		. .	. .	0·52	0·04	. .	
Sulphur		. .	. .	. .	trace	. .	
Phosphorus		. .	. .	. .	. .	0·02	
Residue	Iron	1·50	1·48	0·10	0·234	1·802	0·75
	Nickel	0·39*	0·34	0·04	0·088	0·183	0·33
	Phosphorus	0·32	0·32	0·01	0·112	0·068	0·16
	Copper	. .	0·04	0·01			
	Tin	. .	0·03	0·01			
	Magnesium	. .	. .	. .	0·046	. .	Cr 0·04
	Sulphur	. .	. .	trace	. .	. .	SiO^2 0·01
	Carbon	. .	. .	0·01	. . .	0·175	0·01
		100·00	100·00	100·00	100·00	99·188	100·00

	7.	8.	9.	10.	11.	12.	13.	14.	15.
Analyst.	Smith.	Field.	Forchhammer.	Uricoechea.	Uricoechea.	Pugh.	Pugh.	Bergemann.	Hugo Müller.
Iron	85·54	87·80	93·39	81·20	90·40	90·43	87·89	85·42	90·91
Nickel	8·55	11·88	1·56	15·09	5·02	7·62	9·05	9·73	5·65
Cobalt	0·61	. .	0·25	2·56	0·04	0·72	1·07	0·44	0·42
Copper	0·03	. .	0·45	. .	trace	0·03	trace	0·03	trace
Tin	. .	. .	. .						
Manganese	. .	. .	. .	. .	. .	. .	0·20		
Magnesium	. .	. .	. .	. .	. .	. .	. .	0 19	
Magnesia	2·04	. .	. .	. .	. .	. .	. .	. .	trace
Chromic oxide	0·21								
Sulphur	. .	. .	0·67	. .	trace	0·03	. .	0·84	0·07
Silicium	. .	. .	0·38						
Silica	3·02	. .	. .	. .	. .	. .	. .	. .	0·50
Phosphorus	0·12	0·3	0·18	0·09	0·16	0·15	0·62	. .	0·23
Phosphide of iron and nickel	. .	. .	. .	. .	2·99	0·56	0·34	1·05	
Carbide of iron	. .	. .	. .	. .	. .	. .	. .	0·33	
Chrome-iron	. .	. .	. .	. .	. .	. .	. .	1·48	
Admixed minerals	. .	. .	. .	. .	1·11	0·34	0·22		
Carbon	. .	. .	1·69	. .	. .				
Residue	. .	. .	. .	0·95	. .	. .	. .	. .	2·72
	100·12	99·98	98·57	99·89	99·72	99·88	99·39	199·51	100·50

powder, which afterwards disappears, leaving nothing but carbon. This crystalline powder is not the ordinary phosphide of nickel and iron, but a carbide of iron containing from 7·23 to 11·06 per cent. carbon. The residue insoluble in hydrochloric acid also contains traces of earths reacting like yttria and zirconia.

10. Cape of Good Hope, near the Sunday and Bushman river. Specific gravity = 6·63—7·94 (Rumler); 7·66 (Wehrle). The residue consists, according to Uricoechea, of brownish-yellow and colourless granules; according to Bocking, of phosphide of nickel and iron. This meteorite is one of those which do not exhibit any Widmanstättian figures when etched with acids (p. 378).

* With magnesium.

† With calcium and arsenic.

11, 12, 13. From the Valley of Toluca, near Xiquipilco, in Mexico, where numerous masses of meteoric are found, of various sizes, and often converted into ferric hydrate, even to the middle of their substance. According to Kranz, many of the lumps contain, in cavities on their surfaces, magnetic oxide of iron, both massive and crystallised, and apparently not resulting from recent oxidation; also graphite, sulphide of iron, and laminæ of nickel-iron-phosphide.

Analysis 11 is of a lump weighing 13 lbs., which gave off sulphydric acid when dissolved; 12 of a mass weighing 220 lbs., much oxidised; 13 of a less oxidised mass weighing 5½ lbs.

14. Zacatecas in Mexico, with sulphide of iron disseminated through it. Specific gravity = 7·48 (Bergemann); 7·35 (Rumler). Dissolves in hydrochloric acid, with evolution of fetid hydrogen gas.

15. Also from Zacatecas. Soft, tough, difficult to break, with distinctly laminated structure on the surface. The residue, insoluble in dilute hydrochloric acid, consists of a small quantity of a black flocculent substance resembling graphite, but dissolving in strong hydrochloric acid with evolution of sulphydric acid,—and of nickel-iron-phosphide containing 75·02 Fe, 14·52 Ni, and 10·23 P. Müller (Chem. Soc. Qu. J. xi. 236) regards this meteorite as distinct from that from the same locality analysed by Bergemann (14), inasmuch as the latter contains neither carbon nor chrome-iron.

2. **Meteoric Stones.**

This name, as already observed, is applied to meteorites consisting wholly, or for the most part, of earthy minerals (silicates). The older analyses of these stones by Howard, Klaproth and others, determined merely the entire chemical constitution without regard to the possible existence of different minerals in the same stone; but the later researches of Berzelius, Gustav Rose, Rammelsberg, &c., have shown that meteoric stones are mixtures of certain silicates, viz. olivin, augite, labradorite, &c., with or without meteoric iron. In some few cases, the mineralogical constituents of a meteorite can be distinguished by physical examination; thus Gustav Rose showed that the meteorite of Juvenas contains magnetic pyrites, augite, and a felspar resembling labradorite, and determined the form and other properties of these minerals. But generally speaking, the individual constituents of the meteorite are not recognisable by the sight, even on microscopical examination, and can only be determined by chemical analysis. If the stone contains only two minerals, one of which is decomposible by acids, while the other is not, the determination of their nature is comparatively easy and certain; but if both are attacked by acids with equal facility, or not attacked at all, or if the stone is a mixture of three or more minerals, chemical analysis can only show what minerals *probably* exist in it.

The following are examples of meteoric stones whose constitution has been most accurately determined:

a. *Containing Meteoric Iron.*

1. Chantonnay, Depart. Vendée. Fell on August 5, 1812. Ground-mass partly black, partly grey, with black streaks. Specific gravity = 3·46—3·48 (Rumler). The silicates of this meteorite consist of 51·12 per cent. olivin, 38·01 augite, and 10·01 labradorite (= 99·16). (Rammelsberg.)

2. Seres in Macedonia. Fell in June 1818. Dark grey mass, of specific gravity 3·71 (Rumler). Consists of a mixture of silicates, in which are imbedded a mineral resembling olivin, nickel-iron, and magnetic pyrites. (Berzelius.)

3. Blansko in Moravia. Nov. 25, 1833. Dark grey; specific gravity = 3·70 (Rumler). From an analysis by Berzelius, Rammelsberg calculates the composition at 20·13 per cent. nickel-iron, 2·97 sulphide of iron, 0·63 chrome-iron, 35·18 olivin, 33·89 augite, and 17·30 labradorite.

4. Chateau-Renard, Depart. Loiret, in France. June 12, 1841. Grey; specific gravity = 3·56 (Dufrénoy); 3·54 (Rammelsberg). Consists, according to Dufrénoy, of 50 per cent. olivin, and about 10 per cent. nickel-iron, the remainder appearing to be made up chiefly of augite and labradorite.

5. Utrecht (Louvenhautje near). June 2, 1843. Ground-mass nearly white, fusible. Specific gravity, 3·57—3·65 (Baumhauer). Consists, according to Baumhauer, of a mixture of olivin, augite, oligoclase, nickel-iron (10 per cent.), and magnetic pyrites.

6. Klein-Wenden, near Nordhausen in the Harz. Sept. 16, 1843. Grey ground-mass, intermixed with yellowish-green and black grains. Specific gravity = 3·7006 (Rammelsberg). Consists, according to Rammelsberg, of olivin, augite, and labradorite, in which are imbedded nickel-iron (about 20 per cent.), and a small quantity of pyrites (magnetic pyrites or protosulphide).

7. Montréjeau (Clarac, Ausson), Depart de la Haute-Garonne. December 9,

1858. Greyish-white ground-mass, interspersed with numerous brownish round granules of various sizes, and greyish-white magnetic metallic granules and laminæ. Specific gravity = 3·30. (Filhol and Lemeyrie); 3·50 (Chancel and Moitessier). Contains, according to the latter, 10·04 per cent. matter attracted by the magnet (= 8·36 Fe, 1·56 Ni, 0·07 metallic phosphides, 0·05 adhering ferrous sulphide), 1·71 chrome-iron, 5·72 ferrous sulphide, 45·08 olivin, and 37·51 felspar and hornblende. (Jahresb. 1859, p. 850.)

β. *Without Meteoric Iron.*

1. Stannern in Moravia. May, 22, 1808. Specific gravity = 3·19 (Vauquelin); 3·01—3·17 (Rumler). Consists, according to Rammelsberg, of 65·15 per cent. augite, 34·92 anorthite, 0·98 magnetic oxide of iron, and 0·54 chrome-iron (= 101·59). The augite contains 1 at. magnesium to 2 at. calcium and 3 at. iron.

2. Juvenas, Dept. Ardêche, France. June 3, 1821. Specific gravity = 3·11 (Rumler). Consists, according to Rammelsberg, of 62·65 per cent. augite, 34·56 anorthite, 0·60 apatite, 0·25 titanite, 1·35 chrome-iron, 1·17 magnetic oxide of iron, and 0·25 magnetic pyrites (= 100·83).

3. Jonzac, near Barbezieux, Dept. de la Basse-Charente, France. June 13, 1819. Specific gravity = 3·08 (Rumler). Resembles the preceding in properties and composition.

4. Lontalax, near Wiborg, in Finland. December 13, 1813. Specific gravity = 3·07 (Rumler). Contains, according to Berzelius, magnetic iron ore, and silicates, of which 93·55 per cent. consist of a silicate decomposible by nitro-muriatic acid, and having the composition of olivin (containing 1 at. iron to 2 at. magnesium), with traces of copper, tin, and alkali-metals, and 6·45 of a silicate of aluminium, iron, manganese, and calcium, the composition of which has not been determined; also a small quantity of chrome-iron.

5. Bishopsville, South Carolina. March 1843. A very peculiar stone, consisting for the most part of a white mineral partly crystallised and apparently monoclinic. Specific gravity = 3·116 (Shepard); 3·039 (Waltershausen). Melts before the blowpipe to a white enamel. Contains also small quantities of magnetic pyrites and ferric oxide imbedded in the mass. An analysis of the white mineral by Waltershausen gave 67·14 per cent. silica, 1·48 alumina, 1·70 ferric oxide, 27·11 magnesia, 1·82 lime, and 0·67 water, whence it appears to consist essentially of chladnite, $2Mg^2O.3SiO^2$.

A mineral, perhaps identical with this, obtained from a mass of iron said to be from the neighbourhood of Grimma, was described 30 years ago by Stromeyer.

6. Concord, New Hampshire. White porous mass, which melts on the edges before the blowpipe, colouring the flame yellow. Contains, according to B. Silliman, 84·97 per cent. silica, 12·07 and 2·22 soda, an unusual composition which may be represented by the formula $Na^2O.4SiO^2 + 9Mg^2O.4SiO^2$; considered doubtful by Rammelsberg.

7. Bokkeveld, Cape Colony. October 13, 1838. Soft black mass with a few lighter points. Emits a bituminous odour when heated, and contains a resinous or waxy substance soluble in alcohol, which easily melts and chars. When ignited in contact with the air, even after being freed from the resinous substance, it burns and gives off a quantity of carbonic anhydride equivalent to 1·6 per cent. carbon. It therefore contains carbon, to which in fact its black colour is due. It contains water, even after drying at 100°. It also yields when heated a small quantity of sublimate containing sulphate of ammonium. It acts but slightly on the magnetic needle, and therefore contains but little magnetic iron. It contains 3·8 per cent. sulphur, but does not give off any sulphur when heated, or evolve sulphydric acid gas when treated with hydrochloric acid: hence it cannot contain either iron pyrites, magnetic pyrites, or ferrous sulphide. Wöhler considers the sulphur as belonging to a sulphide of nickel and iron, $Ni^2S.Fe^4S^3$, which requires 1·3 nickel to 2·5 iron, quantities agreeing with those found by analysis. From an analysis by Harris, made under Wöhler's direction, Rammelsberg concludes that the stone contains 6·94 per cent. nickel-iron-sulphide, 1·11 chrome-iron stone, 84·32 olivin, 5·46 undecomposible silicates, and 1·92 carbon and bituminous matters.

8. Kaba, near Debreczin, in Hungary. April 15, 1857. Dark grey, earthy ground-mass, containing white and greenish grains, resembling olivin, also numerous black spherules, very brittle, hollow within, and consisting of a colourless crystalline mineral and a black mineral. The ground-mass exhibits nothing metallic, but yields a small quantity of iron to the magnet. Its composition, according to Wöhler's analysis, is similar to that of the preceding, with addition of 3·55 per cent. magnetic pyrites. When ignited in oxygen gas, it gives off carbonic anhydride, together with a little water and a crystalline sublimate. Alcohol extracts from it a white carboniferous substance resembling paraffin and scheererite, very fusible, partly volatile, partly decomposed by

heat, with separation of carbon. When the pulverised stone, freed from this substance by alcohol, is ignited in oxygen, it turns brown and gives off water, even after it has been well dried.

9. Alais, Dept. du Gard, France. May 15, 1806. Black friable mass, which breaks up in water to a greyish-green pulp, having a strong argillaceous odour, and becomes covered with saline efflorescences when exposed to the air. Water dissolves out 11·5 per cent. of the stone, consisting chiefly of alkaline and earthy sulphates resulting from oxidation of sulphide of iron contained in the stone. The powder, after exhaustion with water, yields by distillation 0·96 per cent. grey sublimate, 4·33 carbonic anhydride, 6·58 water, and 88·15 fixed residue, consisting of effloresced olivin and partially oxidised magnetic iron ore, together with a silicate undecomposible by acids, and containing magnesia and ferrous oxide, with small quantities of alumina, nickel, tin, and copper.

From all that is at present known respecting the constitution of meteorites, Rammelsberg draws the following conclusions:—

Meteoric iron consists of an alloy of iron and nickel (the latter generally amounting to 6—9 per cent., or 1 at. nickel to 10—15 at. iron) mixed with nickel-iron-phosphide or *Schreibersite*, sulphide of iron, carbon, carbide of iron, and chrome-iron, sometimes also with olivin and magnetic oxide of iron.

Meteoric stones. (*a*.) Most of them contain more or less meteoric iron, imbedded in a ground-mass, probably consisting of olivin, augite, and labradorite. Stones of this class are rich in iron and magnesium, poor in calcium and aluminium.

(*b*.) A smaller number, containing no meteoric iron, may be subdivided into—

α. Containing *olivin*. These consist of olivin probably with augite and labradorite, and contain magnetic oxide of iron, sulphide of iron (meteorites of Lontalax, Bokkeveld, Kaba, Alais).

β. Not containing *olivin*. They consist of augite and anorthite, together with small quantities of sulphide of iron, magnetic oxide of iron, and chrome-iron (meteorites of Stannern, Juvenas, Jonzac). They are rich in calcium and aluminium.

γ. The meteorite of Bishopsville consists mainly of a silicate called *chladnite*, having the composition $2Mg^2O.3SiO^2$.

Shepard (Sill. Am. J. [2] ii. 377; vi. 402; xv. 363) mentions also a number of other minerals, some of them quite new, as existing in meteorites; but their existence is by no means satisfactorily established.

Meteorites are covered over their entire surface, except where recently fractured, with a thin black, more or less shining crust, which, on closer examination, presents a fused slag-like appearance. It is doubtless produced by the strong but transient heating which the meteorite undergoes during its rapid transit through the earth's atmosphere. This rise of temperature, which is further indicated by the luminosity of those meteorites whose fall has been observed, and by the fact that some of them, on reaching the earth, have been found in a heated and even incandescent state, may be attributed, in part at least, to the friction of the stone against the particles of the air which it meets in its rapid passage.

Liquid or gelatinous masses called meteoric mud (*Meteorschleim*) have sometimes been observed to fall; but their chemical constitution has not been examined: they are said indeed to consist of volatile substances which cannot easily be preserved, and altogether the accounts respecting them are very vague and unsatisfactory. A mass of this kind which fell near Gotha in the year 1815, is described as of gelatinous consistence and of dark grey colour by moonlight. It smelt like liver of sulphur, and when held in the observer's hand, melted to a thick liquid which quickly evaporated, diffusing a strong odour like that of burning sulphur and phosphorus. (Handw. d. Chem. v. 224.)

The so-called meteoric dust (*Meteorstaub*), which has sometimes been observed to fall from the air on ships at a considerable distance from land, is in all probability of terrestrial origin. Gibbs (Pogg. Ann. lxxi. 367) found in a specimen of such dust which fell on a ship in the Atlantic Ocean (after deduction of 18·53 per cent. water and organic matter), 45·58 per cent. silica, 20·55 alumina, 9·39 ferric oxide, 4·22 manganic oxide, 11·77 calcic carbonate, 2·21 magnesia, 3·645 potash, 2·33 soda, and 0·31 cupric oxide. Ehrenberg has detected infusoria in some specimens of supposed meteoric dust, and supposes that it is transported from one part of the earth to another by violent storms. It may sometimes also be of volcanic origin (i. 420).

For further details respecting the chemical constitution of meteorites, see Rammelsberg's *Mineralchemie* (pp. 901–952).

On the physical and chemical constitution, classification, &c. of meteorites, see the following works:

Partsch.—*Die Meteoriten, oder die vom Himmel gefallenen Steine und Eisenmassen, im k. k. Hof-Mineralien Cabinette zu Wien*, 1843.

C. U. Shepard.—*Report on American Meteorites* (from Silliman's Journal), Newhaven, 1848.

Reichenbach.—*Anordnung und Eintheilung der Meteoriten* (Poggendorff's Annalen, 1859, cvii. 155).

E. P. Harris.—*The Chemical Constitution and Chronological Arrangement of Meteorites*, Dissertation, Göttingen, 1859.

Gustav Rose.—*Beschreibung und Eintheilung der Meteoriten auf Grund der Sammlung im mineralogischen Museum zu Berlin* (aus den Abhandlungen der königl. Academie der Wissenschaften zu Berlin, 1863), Berlin, 1864.

A chronological list of meteorites from the earliest records down to A.D. 1824, is given in the *Annales de Chimie*, tome xxx., and in Ure's *Dictionary of Chemistry*, 3rd. ed., pp. 619–624.

METHAL. Syn. with Myristic Alcohol.

METHIDE, ALUMINIC. $AllC^3H^9$, or $AllMe^3$. (Buckton and Odling, Proc. Royal Soc. xiv. 19.) When mercuric methide and excess of aluminium clippings contained in sealed tubes are heated for some hours in a water-bath, the mercury completely replaces the aluminium, thus:

$$3HhgMe^2 + All^2 = 2AllMe^3 + Hhg^3.$$

By rectification out of contact with air, the aluminic methide is obtained as a colourless mobile liquid, which at a little above 0° congeals into a transparent crystalline mass. It boils steadily at 130°. At and above 220° its vapour-density was found to be 2·8, the theoretical density calculated for the formulæ $AllMe^3$ being 2·5. But its density corrected for expansion, increases rapidly with every decrease of temperature, so that at 160°—163° it becomes 3·96 or 4·1; while at its boiling point 130°, it is as high as 4·4, which approximates to the theoretical density 5·0 calculated for the formula All^2Me^6. Aluminic methide takes fire spontaneously on exposure to air, burning with a very smoky flame and producing abundant flocculi of alumina discoloured by soot. By a regulated exposure to dry air, it absorbs oxygen, with production of a body apparently analogous to boric dioxymethide (p. 986). It is decomposed by water with explosive violence, and reacts with iodine to form iodo-derivatives and iodide of methyl.

Aluminic ethide, $AllE^3$, is made by a precisely similar process, using mercuric ethide instead of mercuric methide. It is a colourless liquid which does not solidify at −18°. It boils at 194°, and its vapour-density taken at 234° was found to be 4·5, the theoretical density calculated for the formula $AllEt^3$ being 3·9. The excess of the experimental over the calculated density was obviously due to some unavoidable oxidation of the substance examined. Aluminic ethide takes fire spontaneously on exposure to air, and in its other chemical properties closely resembles the methyl compound. Cahours (Ann. Chim. Phys. [3]. lviii. 5) observed that aluminium was attacked by the iodides of methyl and ethyl at 100°—130°, and that the crude ethylated product reacted violently with zinc-chloride to form a very inflammable liquid which was doubtless aluminic ethide.

It is worthy of note, that the vapour-volumes of aluminic ethide ($AllE^3$ = 2 vols.), and of aluminic methide at 220° and upwards ($AllMe^3$ = 2 vols.), are discordant with the vapour-density of aluminic chloride as determined by Deville ($AllCl^3$ = 1 vol.); but that the vapour-volume of the methide taken at 130° corresponds very nearly therewith. Hence it would seem that the only observed volume of the chloride, like the volume of the methide at 130°, is anomalous, probably in consequence of its vapour not having been sufficiently heated to acquire that perfection of elasticity under which alone the bulk of a vapour is regulated by the physical laws of temperature and pressure affecting gases. W. O.

METHIDE, BORIC. See Methyl, Boride of (p. 384).

METHIDE, MERCURIC. See Mercury-radicles, Organic (p. 927).

METHIDES, PLUMBIC. See Lead-radicles, Organic (p. 503).

METHIDES, STANNIC. See Tin-radicles, Organic.

METHIONIC ACID. An acid obtained by decomposing neutral sulphate of ethyl with water (Liebig). It has been shown by Buckton and Hofmann (Ann. Ch. Pharm. c. 163) to be identical with disulphometholic acid, $CH^4S^2O^6$. (See Sulphurous Ethers.)

METHOXACETIC ACID. Syn. with Methyl-glycollic Acid. (See Glycollic Ethers, ii. 916.)

METHPLUMBETHYL. Syn. with Plumbotrimethyl. (See Lead-radicles, Organic, p. 563.)

METHSTANNETHYL. See Tin-radicles, Organic.

METHULMENE, AND METHULMIC ACID. (E. Hardy, Bull. Soc.

Chim. de Paris, 1862, p. 29, Jahresb. 1862, p. 388.) These are brown uncrystallisable substances, resembling the ulmic compounds, produced by the action of sodium and methylic alcohol on chloroform. The immediate products of the reaction are chloromethulmic acid and its sodium-salt, together with marsh-gas, carbonic anhydride, free hydrogen, and chloride of sodium:

$$\underset{\text{Chloroform.}}{4CHCl^3} + \underset{\text{Methylic alcohol.}}{6CH^4O} + Na^{11} = \underset{\text{Chloromethulmic acid.}}{C^5H^7ClO^2} + \underset{\text{Chloromethulmate of sodium.}}{C^5H^6NaClO^2} + CH^4 + CO^2 + H^{11} + 10NaCl.$$

Chloromethulmic acid is black, semifluid, has a pungent odour, and is soluble in alcohol.

By boiling with *potash*, it is resolved into methulmic acid, $C^5H^8O^2$, and dioxymethulmic acid, $C^5H^8O^4$:

$$2C^5H^7ClO^2 + 2KHO = 2KCl + C^5H^8O^2 + C^5H^8O^4.$$

Methulmic acid is dark yellow, soluble in ether, uncrystallisable, It is converted by *bromine* into black, semi-fluid dibromomethulmic acid, $C^5H^6Br^2O^2$, which when treated with *sulphuric acid* at 60°, is resolved into carbonic anhydride and dibromide of hypomethulmene, $C^4H^6Br^2$, a yellow-brown solid substance, soluble in ether.

Dioxymethulmic acid, $C^5H^8O^4$, is black, uncrystallisable, insoluble in ether, soluble in alcohol.

Chlorethulmic acid, $C^6H^9ClO^2$, and chloramylulmic acid, $C^9H^{15}ClO^2$, are produced in like manner by treating chloroform with sodium and ethylic or amylic alcohol, and from these may be obtained derivatives similar in properties and homologous in composition to the methyl-compounds above described.—Dibromethulmic acid, $C^6H^8Br^2O^2$, heated to 60° with *sulphuric acid*, is resolved into carbonic anhydride and dibromide of methulmene, $C^5H^8Br^2$, a brown-yellow substance, nearly insoluble in alcohol, but soluble in ether. It is converted by fuming *nitric acid* into pale yellow nitrobromide of methulmene, $C^5H^8(NO^2)Br$, precipitable by water, and by boiling *potash-lye* into bromomethulmene, C^5H^7Br, a black substance insoluble in acids and in alcohol, soluble in ether.

Compounds similar to the preceding are said to be formed by treating chloroform with sodium in conjunction with aldehydes, acetones, &c., and even when the chloroform is replaced by certain other compounds, especially the chlorides of carbon. It must be observed, however, that the composition of the majority of the compounds above mentioned has not been established by analysis, and therefore their formulæ must be considered doubtful, especially as none of them have been obtained in the crystalline form.

METHYL. CH^3; often denoted by the shorter symbol, Me; in the free state, $C^2H^6 = Me^2$. The first of the series of alcohol-radicles, C^nH^{2n+1}, bearing the same relation to wood-spirit that ethyl (C^2H^5) bears to common alcohol.

Frankland and Kolbe, in 1848 (Chem. Soc. Qu. J. i. 60), by decomposing cyanide of ethyl with potassium, first obtained a gas having the composition CH^3 or C^2H^6, which they regarded as methyl. Kolbe, in the following year (*ibid.* ii. 173), obtained methyl by the electrolysis of acetic acid; and Frankland (*ibid.* ii. 297) afterwards prepared it by the action of zinc on iodide of methyl. From certain differences which he observed in the action of chlorine on the gas obtained by the first method, and that obtained by the second and third methods, Frankland concluded that the two were not identical but only isomeric, and that the latter was the true methyl, while the former consisted of hydride of ethyl, $C^2H^5.H$; but the recent experiments of Schorlemmer (*vid. inf.*) have shown that the products obtained by the action of chlorine on the gases prepared by these several methods are really the same; whence, as no other difference has yet been observed between the two, it may be inferred, as most probable, that methyl in the free state is not only isomeric, but identical, with hydride of ethyl. (See HYDRIDES, p. 182.)

Preparation.—1. *By the electrolysis of Acetic acid.*—When a concentrated solution of acetate of potassium is subjected to the action of the electric current, a number of gaseous products are evolved, viz. carbonic anhydride, hydrogen, an inflammable, inodorous gas, and a gas which smells like ether; the last is completely absorbed by sulphuric acid (if the smallest quantity of chloride of potassium be present in the solution, chloride of methyl is formed). The gaseous mixture thus evolved, after being freed from carbonic anhydride, contained in one experiment, in 100 volumes: 0·7 vol. oxygen, 63·8 hydrogen, 32·6 methyl, 2·1 oxide of methyl, 0·8 acetate of methyl; in another experiment, 66 vol. hydrogen were obtained to 28 methyl. If the solution of acetate of potassium be divided by a porous diaphragm, so that the gases evolved at the two poles may be collected separately, nothing but hydrogen is evolved at the negative pole, while at the positive pole there is evolved a gaseous mixture, which, after being treated with potash and with sulphuric acid, leaves nothing but methyl mixed with a small quantity of oxide of methyl. The decomposition is expressed by the following equation:

$$2C^2H^3KO^2 + H^2O = C^2H^6 + CO^2 + K^2CO^3 + H^2.$$

2. By decomposing *iodide of methyl* with *zinc*, the mode of operating being exactly similar to that already described for the preparation of ethyl from ethylic iodide (ii. 524).

If methyl be really identical with hydride of ethyl, we must add to these methods those already given for the preparation of the latter (ii. 533). Schorlemmer prepares it by the action of strong sulphuric acid on mercuric ethide (p. 925).

Properties.—Methyl is a colourless and odourless gas which burns with a bluish feebly luminous flame. It is somewhat soluble in *alcohol*, less soluble in *water* (see GASES, ABSORPTION OF, ii. 797). It is perfectly indifferent to the greater number of reagents. When mixed, either in the moist or dry state, with an equal volume of *chlorine*, it yields hydrochloric acid and chloride of ethyl, C^2H^5Cl, together with a small quantity of monochlorinated chloride of ethyl, $C^2H^4Cl^2$ (Schorlemmer, Proc. Roy. Soc. xiii. 225). These results were obtained with methyl prepared by the electrolysis of acetic acid; and exactly the same products are formed by the action of chlorine on pure hydride of ethyl prepared by the action of sulphuric acid on mercuric ethide (Schorlemmer, Chem. Soc. J. xvii. 962). If the chlorine is used in excess, a larger quantity of the monochlorinated chloride of ethyl is obtained.

METHYL, ANTIMONIDES OF. See ANTIMONY-RADICLES, ORGANIC (i. 344).

METHYL, ARSENIDES OF. See ARSENIO-RADICLES, ORGANIC (i. 400).

METHYL, BORIDE OF. *Boric Methide. Bormethyl.* $B(CH^3)^3$. (Frankland, Phil. Trans. 1862, p. 176; Chem. Soc. Qu. J. xv. 373.)—A gaseous compound homologous with boride of ethyl (ii. 525), produced by the action of zinc-methyl on borate of ethyl:

$$\underset{\substack{\text{Triethylic}\\\text{borate.}}}{B(C^2H^5O)^3} + \underset{\substack{\text{Zinc-}\\\text{methyl.}}}{3CH^3Zn} = \underset{\substack{\text{Boric}\\\text{methide.}}}{B(CH^3)^3} + \underset{\substack{\text{Ethylate}\\\text{of zinc.}}}{3C^2H^5ZnO.}$$

Preparation.—About two ounces of boric ether were mixed in a small flask with rather more than their own bulk of an ethereal solution of zinc-methyl, of such strength as to be spontaneously inflammable in a high degree. The flask, loosely corked, was placed in ice-cold water, and allowed to stand for a couple of hours until the reaction was complete: it was then furnished with a bent tube passing through a cork, to conduct the gas into a second flask placed in a freezing mixture of ice and salt; from this flask the gas passed into a third containing about half an ounce of strong solution of ammonia. The air in the whole of the apparatus was now displaced by nitrogen, and the flask containing the boric ether and zinc-methyl removed from the ice-cold water. A slow evolution of gas immediately commenced, and was kept up at a convenient speed by plunging the generating flask into cold water, to which heat was very slowly applied. The gas, in passing through the freezing mixture, deposited nearly the whole of the ether and zinc-methyl vapour with which it was contaminated; and on reaching the solution of ammonia, the boron-compound was instantaneously absorbed, whilst other gases, if present, passed through the ammonia unacted upon, and escaped into the atmosphere. The solution of ammonia soon became covered with a stratum of a lighter liquid, which increased in quantity until the stream of gas ceased to pass through. The ammonia-flask was now disconnected from the rest of the apparatus, and reserved for the next operation. The residue in the generating flask solidified to a crystalline mass on cooling.

To disengage the gaseous boron-compound from its combination with ammonia, the ammonia-flask was fitted with a funnel-tube terminating beneath the surface of the liquid, and a gas-delivery tube, the latter leading to a Liebig's potash-apparatus charged with concentrated sulphuric acid; finally, the opposite extremity of the latter apparatus was connected with a mercurial gas-holder. To prevent dangerous explosions, on the elimination of the spontaneously inflammable gas from its ammonia-compound, the whole of the air-spaces of the apparatus were filled with nitrogen. Everything being thus prepared, dilute sulphuric acid was gradually poured into the ammonia-flask through the funnel-tube, the contents of the flask being frequently agitated. No gas was evolved until the excess of ammonia was saturated; then, however, it was given off abundantly, and the addition of a few drops of sulphuric acid, from time to time, through the funnel-tube, served to keep up a convenient current. The gas was allowed to pass freely through the depressed mercurial gas-holder until a sample of it proved, by its perfect solution in ammonia, that all nitrogen had been swept from the apparatus.

The exit-tube of the gas-holder was then closed, and the gaseous boric methide was collected.

Properties.—Boric methide is at ordinary temperatures a colourless and transparent gas, possessing a peculiar and intolerably pungent odour, irritating the mucous membrane, and provoking a copious flow of tears. Its specific gravity is by experiment, 1·9108; by calculation, 1·93137. It retains its gaseous condition when exposed to a cold of 16°; but at 10°, and under a pressure of three atmospheres, it condenses to a colourless, transparent, and very mobile liquid. It is very sparingly soluble in *water*, but very soluble in *alcohol* and in *ether*. In contact with *atmospheric air*, it takes fire spontaneously, burning with a bright green flame, which is very fuliginous if the volume of the flame be considerable. If the gas issues into the air through a tube $\frac{1}{10}$ of an inch in diameter, the amount of smoke is surprisingly great, two or three cubic inches of gas, when consumed in this way, filling the atmosphere of a capacious room with large comet-like flocks of carbonaceous matter. This effect is probably due, in part at least, to the formation of a superficial coating of boric acid, which envelopes the particles of carbon and prevents their combustion. When suddenly mixed with *atmospheric air* or *oxygen*, boric methide explodes with great violence. In contact with air, both boric methide and the vapour of boric ethide exhibit two distinct kinds of spontaneous combustion. Thus, when these bodies issue very slowly from a glass tube into the air, they burn with a lambent blue flame invisible in daylight, and the temperature of which is so low that a finger may be held in it for some time without much inconvenience. Under these circumstances partial oxidation only takes place, and it is to the products thus formed that the peculiar pungent odour of boric ethide and boric methide is due. When, on the other hand, these bodies issue into the air more rapidly, the lambent blue and nearly cold flame changes to the green and hot flame above mentioned.

Boric methide is not acted upon by *nitric oxide* or by *iodine*. Solution of *acid chromate of potassium* scarcely affects it, but the addition of concentrated sulphuric acid at once determines the reduction of the chromic acid. When boric methide is allowed to bubble through water into *chlorine*, each bubble burns explosively with a bright flash of light and separation of carbon. It has no tendency to unite with *acids*. Concentrated sulphuric acid has no action upon it; when mixed with hydriodic acid gas, it suffers no change; but, on the other hand, it is freely absorbed by solutions of the fixed *alkalis*, and by *ammonia*. If a very rapid current of the gas, mixed with half its volume of marsh-gas, be passed through a stratum of strong solution of ammonia only half an inch deep, not a trace of boric methide escapes absorption.

Ammonia-Boric Methide. $NH^3.B(CH^3)^3$.—When dry ammoniacal gas is mixed with an equal volume of dry boric methide, both gases instantly disappear, with evolution of a considerable amount of heat, and production of a white, volatile, crystalline compound. The latter is also formed when boric methide is passed into solution of ammonia.

It is deposited from its ethereal solution in magnificent arborescent crystals, which rapidly volatilise without residue when exposed to the air. They have a caustic and bitter taste, and a very peculiar odour, in which both the smell of ammonia and of boric methide can be recognised. Ammonia-boric methide fuses at 56°, and boils at about 110°. In a current of air, or better, of carbonic anhydride, it sublimes at a very gentle heat, and condenses in magnificent arborescent crystals.

Its vapour-density is found by experiment to be 1·25, indicating that the molecule in the state of vapour occupies four volumes $\left(\frac{17 + 11 + 3 . 15}{4} \times 0·0693 = 1·26\right)$, a result probably due, as in other cases, to the decomposition of the vapour at high temperatures (i. 469; ii. 816).

It scarcely absorbs a perceptible amount of *oxygen* at ordinary temperatures, even after several days' exposure to the gas, but takes fire below 100°, when heated in contact with the air. Its vapour is also very inflammable; thus when ammonia-boric methide is placed under the receiver of an air-pump, and the air is being withdrawn, the explosion of the mixture of air and vapour in the cylinders of the pump is frequently determined by the rise of temperature consequent upon the depression of the pistons when the rarefaction has become considerable.

Boric methide is also absorbed by *aniline* with great avidity. Acids expel the gas from this compound unchanged.

Trihydride of phosphorus has no action upon boric methide. A mixture of equal volumes of the two gases is spontaneously inflammable, burning with a yellowish-white flame, in which the characteristic green tinge attending the combustion of boric methide is no longer perceptible.

Compounds of Boric Methide with fixed Alkalis.—Boric methide combines with potash, soda, lime, and baryta. The *potassium-compound* $K^2O.2B(CH^3)$, obtained by saturating a solution of caustic potash with boric methide, dries up in vacuo to a gummy mass. It may also be prepared by decomposing ammonia-boric methide with alcoholic potash, and evaporating in vacuo.

The *sodic*, *barytic*, and *calcic* compounds are also prepared by passing boric methide into the caustic solutions of the respective alkalis; they are soluble in water, and have an alkaline reaction.

METHYL, BROMIDE OF. CH^3Br. *Methyl-hydrobromic ether. Hydrobromate of Methylene.* (Pierre, J. Pharm. [3] xiii. 156; Jahresb. 1847–48, p. 672.—Bunsen, Ann. Ch. Pharm. xlvi. 44.)—Prepared by mixing, at a temperature of 5° or 6°, 50 pts. of bromine, 200 of methylic alcohol, and 7 of phosphorus. The temperature then rises spontaneously, and the phosphorus melts. The mixture must be cooled, decanted and very cautiously distilled. As thus obtained, it is a colourless liquid, of penetrating and slightly alliaceous odour; boils at 13° under a pressure of 0·759 met. (Pierre). It acts violently on cacodyl, forming bromide of cacodyl, and bromide of tetramethyl-arsonium (Cahours, Jahresb. 1861, p. 554):

$$2As(CH^3)^2 + 2CH^3Br = As(CH^3)^2Br + As(CH^3)^4Br.$$

A gas having the composition of bromide of methyl, is evolved on gently heating basic perbromide of cacodyl. It has a density of 3·253 (Bunsen, *Gasometry*, p. 121), by calculation, 3·224; a faint ethereal odour, and condenses at −17° into a thin, transparent colourless liquid. It burns with a yellowish flame when mixed with air, and explodes violently with oxygen on the application of flame.

METHYL, CHLORIDE OF. CH^3Cl. *Methyl-hydrochloric ether. Hydrochlorate of Methylene.* (Dumas and Peligot (1835), Ann. Ch. Phys. lxi. 193).—Prepared by heating a mixture of 2 pts. chloride of sodium, 1 pt. of wood-spirit, and 3 pts. of strong sulphuric acid. Chloride of methyl then passes over as a gas, which may be collected over water; it is, however, contaminated with wood-spirit, sulphurous anhydride, and hydride of methyl.

Chloride of methyl is a colourless gas, having an ethereal odour and saccharine taste. Specific gravity 1·736. It does not condense at −18°. Water dissolves 2·8 times its volume of this gas at 16°.

Chloride of methyl burns with a white flame, green at the edges, producing water, hydrochloric acid, and carbonic anhydride. Passed through a red-hot tube, it is resolved, with slight deposition of charcoal, into a mixture of methylene and hydrochloric acid: $CH^3Cl = CH^2 + HCl$ (Dumas and Peligot). According to Perrot (Ann. Ch. Pharm. ci. 375), it deposits charcoal, and yields hydrochloric acid, marsh-gas, ethylene, carbonic oxide, naphthalene, and a substance which unites with bromine into a crystallised compound, melting at 40° and boiling at 220°. When passed over heated *potash-lime*, it yields formate and chloride of potassium, together with hydrogen gas:

$$CH^3Cl + 2KHO = CHKO^2 + KCl + 2H^2.$$

When passed over phosphide of calcium at 200° or 300°, it yields a number of phosphoretted products, some of which appear to be organic bases. (P. Thenard.)

A gas having the same composition and physical properties as the preceding was obtained by Bunsen, by the action of heat on basic perchloride of cacodyl. Kolbe and Varrentrapp (Ann. Ch. Pharm. lxxvi. 37) also obtained a gas of the same composition, by leaving a mixture of equal volumes of marsh-gas and chlorine exposed to diffused daylight. Gerhardt (*Traité*, i. 566) regarded the first only of these products as CH^3Cl, the two latter as $CH^2Cl.H$.

Baeyer (Ann. Ch. Pharm. cvii. 181) finds that the gas produced from basic perchloride of cacodyl, exhibits the same degree of absorbability in water as that produced by heating wood-spirit with salt and sulphuric acid, the coefficient of absorption for both these gases being 5·034 at 7°; 4·172 at 14°; 3·462 at 20°; and 3·034 at 25°. Moreover, the gas obtained by either of these methods forms a crystalline hydrate when passed into water cooled below 6°. On the contrary, the gas produced by the action of chlorine on marsh-gas does not form a crystalline hydrate, and has a much smaller coefficient of absorption in water (0·08 at 14°). Hence Baeyer concludes that the gas produced by the decomposition of basic perchloride of cacodyl is identical with chloride of methyl, but that the gas resulting from the action of chlorine on marsh-gas is a substitution product isomeric but not identical therewith. According to Berthelot, on the other hand, the last-mentioned gas is really chloride of methyl, and may be converted into methylic alcohol by the action of potash.

Chloride of methyl is not attacked by chlorine in diffused daylight, but when exposed to the direct rays of the sun, it yields successively the three compounds—

Monochlorinated Chloride of Methyl	CH^2Cl^2
Dichlorinated Chloride of Methyl, or Chloroform	$CHCl^3$
Trichlorinated Chloride of Methyl, or Tetrachloride of Carbon .	CCl^4

Monochlorinated Chloride of Methyl, $CH^2Cl^2 = C(H^2Cl)Cl$, is a very volatile liquid of exciting odour, similar to that of Dutch liquid. It boils at 30·5°. Specific gravity = 1·344 at 18°. Vapour-density 3·012. Treated with alcoholic potash, it yields but a slight precipitate of chloride of potassium, and distils almost without alteration. (For the other chlorinated compounds, see CHLOROFORM, and CARBON, CHLORIDES OF) (i. 765 and 919).

METHYL, HYDRATE OF. $CH^4O^2 = \left.\begin{matrix}CH^3\\H\end{matrix}\right\}O$. *Methylic Alcohol, Wood-spirit, Wood-naphtha, Pyroxylic spirit, Esprit de Bois, Holzgeist, Holzessiggeist.*—This compound was first observed by Taylor in 1812 (Tilloch's Phil. Mag. lx. 315) among the products of the dry distillation of wood, afterwards more particularly examined by Dumas and Peligot in 1835 (Ann. Ch. Phys. lviii. 5; lxi. 193). It constitutes about 1 per cent. of the watery products of the dry distillation of wood; and in combination with salicylic acid (as methyl salicylic acid), it forms the chief constituent of the essential oil of winter-green (*Gaultheria procumbens*). According to Berthelot (Ann. Ch. Pharm. cv. 241) it may be produced artificially from marsh-gas (that compound when treated with chlorine yielding chloride of methyl, which by boiling with caustic potash is converted into methylic alcohol); and as marsh-gas itself can be formed synthetically from inorganic materials (p. 855), it follows also that methylic alcohol can be obtained by synthesis.

Preparation. 1. *Of Commercial Wood-spirit.*—The crude watery liquid (pyroligneous acid) obtained by the distillation of wood is decanted from the tarry portion of the distillate and redistilled; the first tenth which passes over is rectified, once or oftener over slaked lime, whereupon a large quantity of ammonia is given off; sulphuric acid is then added, which unites with the remaining ammonia and precipitates a certain quantity of tar; and the liquid is redistilled, and finally rectified several times over quicklime.

The crude wood-spirit thus obtained has a strong aromatic odour and turns brown on keeping. It contains considerable quantities of acetate of methyl, acetone, and a liquid called lignone by Weidmann and Schweizer, xylite by Völckel, the nature of which has given rise to considerable discussion, but which has lately been shown by Dancer (Chem. Soc. J. xvii. 222) to consist essentially of dimethyl-acetate of ethylene.

2. *Of Pure Methylic alcohol.* To obtain nearly pure methylic alcohol from commercial wood-spirit, advantage may be taken of the property which it possesses of forming with chloride of calcium a compound which is not decomposed by merely heating it to 100°, but gives off the methylic alcohol when distilled with water. The crude wood-spirit is saturated with fused chloride of calcium, and heated over the water-bath as long as anything volatile is given off; it is thus freed from the acetone, dimethylate of ethylene, &c., which do not unite with the chloride of calcium. The residue is then distilled with water, and the aqueous methylic alcohol thus obtained is rectified over quicklime (Kane, Ann. Ch. Pharm. xix. 164). According to Gould (Chem. Soc. J. vii. 311) it is advisable first to distil the wood-spirit with an equal volume of strong potash or soda-lye, in order to decompose the methylic acetate contained in it, sometimes in very large quantity, then to dehydrate with carbonate of potassium, and finally saturate with chloride of calcium as above.

To obtain perfectly pure methylic alcohol, however, it is necessary first to prepare a methylic ether, and then separate the alcohol from it by distillation with an alkali: *a.* Oxalate of methyl is prepared by distilling 1 pt. wood-spirit, 1 pt. sulphuric acid, and 2 pts. oxalate of potassium; the crystals of this ether, after being purified by pressure, are decomposed by distillation with water, and the distilled methylic alcohol is dehydrated by rectification over quicklime (Wöhler, Ann. Ch. Pharm. lxxxi. 376). *β.* Benzoate of methyl, prepared by passing hydrochloric acid gas into a solution of benzoic acid in wood-spirit, distilling and precipitating the portion collected above 100° with water, is decomposed by several hours boiling with soda-lye, the liquid is then distilled, and the distillate rectified over quicklime.

Methylic alcohol may also be obtained very nearly pure by distilling oil of winter-green (methyl-salicylic acid) with potash or soda-lye, and rectifying the distillate over quicklime; it retains, however, a slight odour of the oil.

Properties.—Methylic alcohol is a colourless mobile liquid, having a purely spirituous odour, like that of common alcohol (the empyreumatic odour of crude wood-spirit arises from the impurities). Specific gravity = 0·8142 at 0°. It boils at 60° to 66·5°, according to the nature of the vessel, and bumps strongly during boiling. It burns with a pale flame, mixes with *water, alcohol,* and *ether,* dissolves oils both fixed and volatile, also the greater number of resins, and is therefore much used as a solvent in place of common alcohol. It is also used for burning in spirit-lamps.

The following table exhibits the strength of pure wood-spirit, according to its density, as determined by Ure (Phil. Mag. [3] xix. 51):

Per-centage of Anhydrous Methylic alcohol (sp. gr. 0·8136, at 15°) *in Wood-spirit.*

Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.
0·8136	100·00	0·8674	82·00	0·9008	69·44	0·9344	53·70
0·8216	98·11	0·8712	80·64	0·9032	68·50	0·9386	51·54
0·8256	96·11	0·8742	79·36	0·9060	67·57	0·9414	50·00
0·8320	94·34	0·8784	78·13	0·9070	66·66	0·9448	47·62
0·8384	92·22	0·8822	77·00	0·9116	65·00	0·9484	46·00
0·8418	90·90	0·8842	75·76	0·9154	63·30	0·9518	43·48
0·8470	88·30	0·8876	74·63	0·9184	61·73	0·9540	41·66
0·8514	87·72	0·8918	73·53	0·9218	60·24	0·9564	40·00
0·8564	86·20	0·8930	72·46	0·9242	58·82	0·9584	38·46
0·8596	84·75	0·8950	71·43	0·9266	57·73	0·9600	37·11
0·8642	83·33	0·8984	70·42	0·9296	56·18	0·9620	35·71

Methylic alcohol unites directly with some substances, forming compounds like the alcoholates (i. 80), in which it takes the place of water of crystallisation. A solution of anhydrous *baryta* in wood-spirit leaves on evaporation crystals containing $Ba^2O.2CH^4O$. *Chloride of calcium* is dissolved by wood-spirit with great rise of temperature, and the solution on cooling deposits large crystals of the compound $CaCl.2CH^4O$, which may be heated to 100° without decomposition, but is decomposed by water, even at temperatures below 100°, yielding a distillate of methylic alcohol.

Decompositions.—1. Vapour of methylic alcohol passed through a red-hot tube yields acetylene, together with other products (Berthelot, Compt. rend. l. 805).—2. Pure methylic-alcohol burns in the *air* with a flame like that of common alcohol, without smoke.—3. In contact with *platinum-black* it is oxidised to formic acid.—4. *Potash* and *soda* dissolve in it readily, forming solutions which turn brown in contact with the air.—5. Methylic alcohol mixed with *sal-ammoniac* and heated in a sealed tube to 300°, yields the hydrochlorates of methylamine, dimethylamine, and trimethylamine (Berthelot).—6. *Hypochlorite of calcium* (bleaching powder) converts it into chloroform ($CHCl^3$). A solution of potash in methylic alcohol treated with *bromine* or *iodine*, yields bromoform or iodoform.—7. With *potassium* it gives off hydrogen and is converted into methylate of potassium, CH^3KO; similarly with *sodium*.—8. Heated with *alkaline hydrates*, it gives off hydrogen and yields a formate of the alkali-metal:

$$CH^4O + KHO = CHKO^2 + H^4.$$

At higher temperatures and with excess of alkali, as when wood-spirit is passed over red hot potash-lime, the formate is converted into oxalate, and ultimately into carbonate, each change being attended with evolution of hydrogen (ii. 688).

9. Strong *sulphuric acid* acts upon methylic, partly in the same manner as upon ethylic-alcohol, producing methyl-sulphuric acid, $CH^3.H.SO^4$, which, when heated in contact with excess of wood-spirit, yields oxide of methyl. The action which takes place at higher temperatures differs, however, from that which takes place under similar circumstances between oil of vitriol and ethylic-alcohol in this respect, that no methylene (CH^2) appears to be produced, but neutral sulphate of methyl, $(CH^3)^2SO^4$, passes over.

10. *Chlorine-gas* passed into anhydrous wood-spirit acts upon it with considerable energy, each bubble of gas sometimes producing flame and detonation, and forms hydrochloric acid, together with several chlorinated products. [The chloracetones sometimes obtained in this reaction result in all probability from acetone contained in the wood-spirit]. According to Cloez (Compt. rend. xlviii. 642; Jahresb. 1859, p. 434) the final product of the action is a crystalline substance, parachloralide, C^2HCl^3O:

$$2CH^4O + Cl^8 = C^2HCl^3O + H^2O + 5HCl.$$

Bromine acts in a similar manner, producing parabromalide, C^2HBr^3O. Riche (Ann. Ch. Pharm. cxii. 323), by subjecting a mixture of wood-spirit and hydrochloric acid to the action of the electric current, obtained a chlorinated liquid containing C^2H^3ClO.

11. When methylic alcohol is added by drops to brown *chloride of sulphur*, SCl^2, a violent action takes place, hydrochloric acid, sulphurous anhydride, and vapour of methylic chloride are evolved, a small quantity of chloride of thionyl, $SOCl^2$, passes over, and the residue, after being heated to 80°, consists of chloride of sulphur, S^2Cl^2. The brown chloride of sulphur, SCl^2, appears indeed to act like a mixture of S^2Cl^2 and

SCl^4, the former remaining unacted upon, while the latter produces the following decomposition:

$$SCl^4 + CH^4O = HCl + SOCl^2 + CH^3Cl$$
$$SCl^4 + 2CH^4O = 2HCl + SO^2 + 2CH^3Cl.$$

Chloride of thionyl also acts violently on methylic alcohol, producing hydrochloric acid and neutral sulphide of methyl, together with chloride of methyl and methyl-sulphurous acid:

$$2SOCl^2 + 4CH^4O = 3HCl + CH^3Cl + (CH^3)^2.SO^3 + CH^3.H.SO^3.$$

Protochloride of sulphur (or *chloride of sulphothionyl*, $SSCl^2$) likewise acts strongly on methylic alcohol, hydrochloric acid and methylic chloride being evolved, while a small quantity of methyl-mercaptan passes over, and the residue contains methyl-sulphurous acid and neutral methylic sulphate, besides separated sulphur. The first reaction is probably

$$S^2Cl^2 + CH^4O = SOCl^2 + CH^4S,$$

and the *chloride of thionyl* then acts on the methyl-mercaptan, and probably also on further quantities of methylic alcohol, as shown by the following equation:

$$3SOCl^2 + 4CH^4S = 4HCl + 2CH^3Cl + (CH^3)^2SO^3 + S^6,$$

and by the last equation but two. (Carius, Ann. Ch. Pharm. cx. 209, cxi. 93.)

Ethyl-sulphurous chloride, $C^2H^5ClSO^2$ (the product of the action of pentachloride of phosphorus on ethyl-sulphites), acts on methylic alcohol (or more definitely on methylate of sodium), producing hydrochloric acid (or chloride of sodium) and methyl-ethyl-sulphurous acid:

$$CH^3.H.O + C^2H^5ClSO^2 = HCl + \left.\begin{matrix}CH^3\\C^2H^5\end{matrix}\right\}SO^3.$$ (Carius, Ann. Ch. Pharm. cxi. 93.)

METHYL, HYDRIDE OF. Syn. with Marsh-gas (p. 854).

METHYL, IODIDE OF. CH^3I.—Obtained by distilling 1 pt. of phosphorus, 8 pts. of iodine, and 12 or 15 pts. of wood-spirit, or according to Hofmann (Chem. Soc. J. xiii. 69), 1000 grms. iodine, 500 methylic alcohol, and 60 phosphorus. The distillate is mixed with water which separates the iodide of methyl, and the product is rectified in the water-bath over chloride of calcium and oxide of lead. It is a colourless liquid, slightly combustible, so that it does not burn well excepting in the flame of a lamp; it then diffuses abundance of violet vapours. Specific gravity = 2·237 at 22°; 2·1992 at 0° (Pierre). Boils at 42·2° under a pressure of 0·752 met. (Andrews); at 43·8° under 0·750 met. pressure (Pierre). Vapour-density = 4·883. It is not attacked by hydrochloric acid gas.

Chlorine converts it into chloride of methyl, with deposition of iodine. Heated with metallic *zinc* in a sealed tube, it yields iodomethylide of zinc:

$$CH^3I + Zn = Zn''CH^3I.$$

Heated with *arsenide*, *antimonide*, &c. of *potassium* or *sodium*, it yields the arsenides antimonides, &c., of methyl. Heated in a sealed tube with *aqueous ammonia*, it forms the iodides of ammonium, methyl-ammonium, di-, tri-, and tetra-methyl-ammonium, the first and last of these iodides being produced in greatest quantity. With *magnesium* it yields magnesic methide (p. 756), the action beginning even at ordinary temperatures; with *aluminium*, aluminic methide (p. 983).

METHYL, OXIDE OF. *Methylic ether.* $C^2H^6O = (CH^3)^2O$. (Dumas and Peligot, Ann. Ch. Phys. [2] lviii. 19.)—Produced by heating a mixture of 1 pt. wood-spirit and 2 pts. strong sulphuric acid, and washing the gaseous product with potash-lye. At ordinary temperatures, it is a gas having a pleasant ethereal odour, very soluble in alcohol, ether, and sulphuric acid, less soluble in water (which dissolves 37 times its volume of the gas at 18°). By cooling to −36°, by means of a mixture of snow and chloride of calcium, it is condensed to a liquid boiling at −20°. (Berthelot.)

Methylic ether unites directly with sulphuric anhydride, forming neutral methylic sulphate, $(CH^3)^2O.SO^3$ or $(CH^3)^2SO^4$.

METHYL, PLUMBIDES OF. See Lead-radicles, Organic (p. 563).

METHYL, SELENIDE OF. *Selenmethyl.* $C^2H^6Se = (CH^3)^2Se$. (Wöhler and Dean, Ann. Ch. Pharm. xcvii. 5.)—Obtained by distilling a solution of methyl-sulphate of barium with selenide of potassium. It is a reddish-yellow very mobile liquid heavier than water, insoluble therein; of intensely disagreeable odour; very inflammable, and burning with a bluish flame. Strong nitric acid dissolves it, with rise of temperature; the solution is not precipitated by hydrochloric acid, but sulphurous acid throws down selenide of methyl from it. On attempting to concentrate the liquid by evaporation, a new and very violent reaction is set up, nitric oxide being evolved, and the temperature sometimes rising so high as to set fire to the mixture.

The product of this reaction is methyl-selenious acid, CH^4SeO^3, which, by cautious evaporation and cooling, may be obtained as a crystalline mass. It forms salts with bases, and is converted by hydrochloric acid into methyl-selenious chloride, $CH^3SeO^2Cl.H^2O$, which crystallises in transparent prisms, and is converted by hydrobromic and hydriodic acid into the corresponding bromine- and iodine-compounds.

METHYL, SULPHIDES OF. Methyl forms three sulphides, represented by the formulæ $(CH^3)^2S$, $(CH^3)^2S^2$ and $(CH^3)^2S^3$, and a sulphydrate or mercaptan, CH^4S, homologous with ethyl-mercaptan.

Protosulphide of Methyl. $C^2H^6S=(CH^3)^2S$. (Regnault, Ann. Ch. Phys. [2] lxxi. 391.)—This compound is easily obtained by passing gaseous chloride of methyl into a solution of protosulphide of potassium in wood-spirit contained in a tubulated retort. The gas is absorbed in large quantity, and if the retort be then heated and the receiver kept cool, sulphide of methyl distils over. It is a colourless, very mobile liquid, having an extremely disagreeable odour. Specific gravity, 0·845 at 21°. Boiling point 41°. Vapour-density 2·115. It is readily attacked by *chlorine*. On letting a few drops of it fall into a bottle filled with dry chlorine, a red flame is produced, and a large quantity of hydrochloric acid is obtained, together with a deposit of charcoal; but if the temperature be kept low, the following substitution-products are obtained:

a. Monochlorinated methylic sulphide, $(CH^2Cl)^2S$. This is the product of the action of chlorine on sulphide of methyl, at a low temperature and under the influence of diffused daylight. It is a yellow oil, heavier than water, and having a very offensive odour. When heated in a retort, part of it distils over, but a considerable portion suffers alteration and leaves a carbonaceous residue. (Riche, Ann. Ch. Phys. [3] xliii. 283.)

β. Dichlorinated methylic sulphide, $(CHCl^2)^2S$. Produced by exposing the preceding compound to the action of chlorine, taking care to cool the vessel at the beginning to prevent the action from becoming too violent. It is a heavy yellow liquid, partly decomposed by distillation. (Riche.)

γ. Perchlorinated methylic sulphide, $(CCl^3)^2S$, is the product of the action of chlorine on the dichlorinated compound under the influence of direct sunshine. It is a limpid, amber-coloured liquid, having a strong penetrating odour. It boils regularly and without alteration between 156° and 160°. Its observed vapour-density is 5·68; the formula C^2Cl^6S gives 9·41 for a condensation to 2 volumes, and 4·7 for a condensation to 4 volumes, indicating dissociation (i. 469); but the specimen operated upon was probably impure. The compound is quite insoluble in water, but dissolves easily in alcohol and ether. It does not appear to be altered by aqueous potash.

The crude liquid resulting from the action of chlorine on dichlorinated methylic sulphide, has a red colour and contains chloride of sulphur and tetrachloride of carbon, which pass over with the first portions of the distillate, and are more abundant in proportion as the dichlorinated sulphide was less completely dried. (Riche.)

Protosulphide of methyl unites, like sulphide of ethyl (ii. 545) with *mercuric chloride* and *platinic chloride*, forming the compounds $C^2H^6S^2.Hhg''Cl^2$ and $C^2H^6S.PtCl^2$, both of which are crystalline.

Disulphide of Methyl. CH^3S or $C^2H^6S^2$. (Cahours, Ann. Ch. Phys. [3] xviii. 157.)—Prepared, 1. By passing gaseous chloride of methyl through an alcoholic solution of disulphide of potassium.—2. By distilling a mixture of sulphomethylate of calcium and disulphide of potassium:

$$2(CH^3)CaSO^4 + K^2S^2 = (CH^3)^2S^2 + Ca^2SO^4 + K^2SO^4.$$

The yellowish distillate is rectified; and the portion which distils over between 110° and 112° is dried by chloride of calcium, and again partially distilled.

It is a transparent colourless liquid, having great refracting power, and a density of 1·046 at 18°. Boils between 116° and 118°. Vapour-density at 196° = 3·298. Has a very persistent and intolerable odour of onions.

It is but very sparingly soluble in *water*, but nevertheless imparts its odour to that liquid. Mixes in all proportions with *alcohol* and *ether*. (Cahours.)

This compound may be set on fire by a red-hot body, and burns with a blue flame, emitting a strong odour of sulphurous acid. *Chlorine* acts violently upon it, producing at first a substance which crystallises in amber-coloured rhombic tables, and is converted, by the further action of the chlorine, into a yellow, and ultimately into a red liquid, consisting of a mixture of C^2Cl^6S and SCl^2. *Bromine* likewise forms substitution-products. Moderately strong *nitric acid* acts strongly on the compound, producing sulphuric acid, and a peculiar acid which forms with potash long slender needles; with baryta, shining colourless tables; and with lime and oxide of lead, soluble crystallisable salts.* *Sulphuric acid* dissolves the compound at ordinary temperatures; but decomposes it when heated. The compound is not altered by distillation over concentrated *potash-solution.*

Trisulphide of Methyl. $(CH^3)^2S^3$.—If the disulphide of potassium in the preceding preparation is replaced by pentasulphide, a considerable quantity of methylic disulphide is likewise obtained, but at the end of the distillation, at about 200°, a yellowish product is obtained having the composition of the trisulphide. It behaves like the disulphide with chlorine and with nitric acid. (Cahours.)

METHYL, SULPHYDRATE OF. $CH^4S = \left.\begin{matrix}CH^3\\H\end{matrix}\right\}S$. (Gregory, Ann. Ch. Pharm. xv. 239.)—Formed by distilling in the water-bath, with efficient condensation, a mixture of 1 pt. of a solution of sulphomethylate of calcium, and 1 pt. of a solution of sulphydrate of calcium (both solutions having a density of 1·25), and agitating the distillate with caustic potash, to free it from sulphydric acid:

$$2(CH^3)CaSO^4 + 2KHS = 2(CH^3.H.S) + K^2SO^4 + Ca^2SO^4.$$

It is a liquid lighter than water, boiling at 21°, and having the odour of mercaptan, but even more offensive. It is slightly soluble in *water;* forms with *acetate of lead* a yellow, and with *mercuric oxide* a white compound (CH^3HgS), which crystallises from a hot alcoholic solution in shining laminæ not fusible at 100°

METHYL, TELLURIDE OF. *Telluro-methyl.* $C^2H^6Te = (CH^3)^2Te$. (Wöhler and Dean, Ann. Ch. Pharm. xciii. 233.—Heeren, *Ueber Telluräthyl- and Tellurmethyl-verbindungen,* Göttingen, 1861.)—This compound is obtained by distilling telluride of potassium with sulphomethylate of barium, the distillation being continued as long as drops of oily liquid pass over with the water, and the process conducted altogether as for the preparation of tellurethyl (ii. 550).

Properties.—Telluromethyl is a pale yellow mobile liquid, which sinks in water, and does not mix with it. It boils at 82°, forming a yellow vapour like tellurium itself. It has an extremely disagreeable alliaceous odour, which is so intense and persistent, that even the breath is affected by it after some time. It fumes in the air from oxidation. When set on fire, it burns with a bright bluish-white flame, diffusing white fumes of tellurous acid. Strong nitric acid oxidises it, with evolution of nitric oxide.

Telluromethyl behaves to oxygen, chlorine and other chlorous radicles, like a metal, forming a basylous oxide and a series of salts, which are produced by saturating the solution of the oxide with acids, or by precipitation.

Acetate of Telluromethyl, $(Me^2Te)''\left\{\begin{matrix}C^2H^3O^2\\HO\end{matrix}\right.$, forms large, well-developed, limpid cubes, which have an unpleasant odour, crumble to a white amorphous powder when exposed to the air, are insoluble in cold alcohol, but dissolve easily in water. The solution is neutral, gives with sulphurous acid a yellow precipitate of telluromethyl; with hydrochloric acid, a white precipitate of the chloride; with iodide of potassium, no precipitate. (Heeren.)

The *bromide,* $(CH^3)^2TeCl^2$ or Me^2TeCl^2, is obtained as a thick white precipitate, resembling bromide or chloride of lead, on adding hydrobromic acid to a solution of nitrate of telluromethyl. It forms shining colourless prisms which melt at 89°. (Wöhler and Dean.)

The *carbonate,* $\left.\begin{matrix}(Me^2Te)''\\(Me^2Te)''\end{matrix}\right\}\begin{matrix}(CO^2)''\\(HO)^2\end{matrix}$, is difficult to crystallise. (Heeren.)

The *chloride,* Me^2TeCl^2, is obtained, on adding hydrochloric acid to a solution of the nitrate, as a thick white precipitate resembling chloride of lead (Wöhler and Dean); as a colourless heavy oil, which solidifies crystalline on cooling; similarly by adding hydrochloric acid to a solution of the oxychloride. (Heeren.)

It redissolves when heated, and crystallises on cooling in long thin prisms, like corrosive sublimate. It appears to be isomorphous with the bromide (Wöhler and Dean). It melts at 97·5°, but appears not to be volatile without decomposition. Solidifies from fusion in a mass having a highly crystalline structure. Does not distil over with water, but its heated aqueous solution has a faint alliaceous odour. Does not form any precipitate with platinic chloride. Dissolves readily in alcohol.

The *formate,* $(Me^2Te)''\left\{\begin{matrix}CHO^2\\HO\end{matrix}\right.$, crystallises in deliquescent colourless needles, forming a neutral solution in water, from which hydrochloric acid precipitates chloride of telluromethyl in the form of a colourless oil. (Heeren.)

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* Muspratt (Chem. Soc. Qu. J. i. 53) gave to this acid the name of *Bisulphimethylic acid,* representing its salts by the formula $C^2H^3MS^2O^5$; more recently, however (Chem. Soc. Qu. J. iii. 22), he has found that it is identical with methyl-sulphurous acid, the formula of whose salts is $C^2H^3MS^2O^6$, or CH^3MSO^3.

Iodide, Me^2TeS^2.—When colourless hydriodic acid, or iodide of potassium, is dropt into a solution of nitrate of telluromethyl, a precipitate is formed of a bright lemon-yellow colour, but changing in a few seconds to vermillion-red. If the solutions are mixed warm, the precipitate exhibits at once a red colour and crystalline structure. When dry, it forms a vermillion coloured powder. The compound dissolves sparingly in cold, much more freely in hot water, and abundantly in hot alcohol, forming a reddish-yellow solution. From both solutions, it crystallises in small shining, vermillion-coloured prisms, which are largest when they separate from the alcoholic solution. They yield an orange-yellow powder. Under the microscope they appear orange-yellow by transmitted light, but certain faces exhibit a fine blue surface-colour. The salt appears to be dimorphous, like iodide of mercury; for on mixing the cooled alcoholic solution with about an equal volume of water, the iodide is precipitated, of a lemon-yellow colour; but in a few minutes a movement of the particles is observed throughout the liquid, and the precipitate soon assumes the character of vermillion-coloured crystalline laminæ. The yellow variety cannot, however, be obtained in a permanent form; for the alcoholic solution yields red crystals by evaporation, and the compound cannot be melted without decomposition. Even at 130°, it is converted into black iodide of tellurium. (Wöhler and Dean.)

Nitrate. $Me^2Te(NO^6)^2$ (Wöhler and Dean); $Me^2Te\left\{\begin{matrix}NO^6\\HO\end{matrix}\right.$. (Heeren.)—Tellurometbyl heated with moderately strong nitric acid, dissolves partially at first, with reddish-yellow colour; but after a while, a violent reaction ensues, attended with evolution of nitric oxide, and a colourless solution of the nitrate is obtained, which by careful evaporation, yields the salt in large colourless prisms. Sometimes, however, probably when the acid is too strong or in too great excess, the salt is obtained on evaporation, not in crystals, but in the form of a transparent amorphous mass containing tellurous acid, mixed or combined, and arising probably from decomposition of a portion of the telluromethyl. The nitrate decomposes with explosion when heated. It dissolves readily in water and alcohol. The aqueous solution, mixed with hydriodic, hydrobromic or hydrochloric acid, yields a precipitate of iodide, bromide or chloride of telluromethyl. (Wöhler and Dean.)

The *oxalate*, $(Me^2Te)^2\left\{\begin{matrix}(C^2O^4)''\\(HO)^2\end{matrix}\right.$, crystallises in monometric forms; it is neutral and less soluble in water than in alcohol; the aqueous solutions give with hydrochloric acid a precipitate of the chloride. (Heeren.)

Oxide of Telluromethyl, Me^2TeO, is obtained by decomposing the chloride or iodide with oxide of silver. Either of these compounds is moistened with water, and oxide of silver, recently precipitated by baryta-water and well washed, is added in excess, whereupon decomposition begins immediately, and the mass becomes spontaneously heated. The filtrate contains the oxide in solution.

Oxide of telluromethyl is indistinctly crystalline when dry; has an abominable taste, but is inodorous; deliquesces in the air like potash, and absorbs carbonic acid. Its aqueous solution is strongly alkaline to test-paper; eliminates ammonia from sal-ammoniac, even at ordinary temperatures, and forms a blue precipitate with sulphate of copper. Sulphurous acid added to the solution immediately throws down telluromethyl, in the form of a stinking oily liquid; hydrochloric acid precipitates the white chloride; hydriodic acid the red iodide. On saturating the aqueous oxide with sulphydric acid, a slight milky turbidity is produced; and on distilling the liquid, white sulphur separates out, and a yellow oil passes over, which appears to be merely reduced telluromethyl (Wöhler and Dean).—Heeren did not succeed in preparing the oxide in the solid state; the strongly alkaline solution obtained by decomposing the oxychloride with recently precipitated silver-oxide, quickly became turbid, and when evaporated in a vacuum, left nothing but tellurium.

The *oxychloride*, $(Me^2Te)^2Cl^2O$, is formed by dissolving the chloride in ammonia. On evaporating and digesting the residue of sal-ammoniac and oxychloride in alcohol, the latter dissolves and separates from the solution in short colourless prisms. Hydrochloric acid added to the solution precipitates the chloride. (Wöhler and Dean.)

The *oxybromide*, $(Me^2Te)^2Br^2O$, is obtained in a similar manner.

Phosphate.—On dropping phosphoric acid into a solution of the oxide, a lemon-yellow precipitate of tellurometbylic phosphate is produced, insoluble in water and in alcohol; it turns grey when exposed to light, and melts when heated to a brown substance (TeP^2?). It dissolves in excess of phosphoric acid, forming a colourless liquid, which yields colourless crystals by evaporation. From the aqueous solution of these crystals, ammonia throws down the yellow insoluble phosphate, and hydrochloric acid the white chloride. (Heeren.)

The *sulphate*, $(Me^2Te)^2\left\{\begin{matrix}SO^4\\(HO)^2\end{matrix}\right.$ (Heeren), is obtained by saturating the base with sulphuric acid, or by decomposing the solution of the oxychloride with sulphate of silver. It crystallises in large, very regular transparent cubes, easily soluble in water, insoluble in alcohol.

Sulphochloride, $(Me^2Te^2)Cl^2S$? Sulphuric acid passed through asolution of the chloride, forms a white flocculent precipitate which afterwards turns yellowish, the liquid at the same time acquiring an extremely repulsive odour. If it be then distilled, there passes over with the water a heavy oily liquid, having a reddish-yellow colour and extremely offensive odour, and yielding sulphuric acid when oxidised with nitromuriatic acid. (Wöhler and Dean.)

According to Heeren, sulphydric acid forms, in solutions of telluromethylic salts, an orange-yellow precipitate, which, when heated or strongly ignited, cakes together, and sinks to the bottom in the form of black heavy oily drops, from which ether extracts telluromethyl, leaving a black powder consisting of disulphide of tellurium.

METHYLACETAL. See METHYLATE OF ETHYLENE.

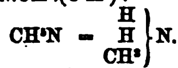
METHYLACETONE. See ACETONE (i. 31).

METHYLAL. $C^3H^8O^2$.—A product of the oxidation of methylic alcohol. When a mixture of wood-spirit, sulphuric acid, and peroxide of manganese is distilled, there passes over, amongst other products, an ethereal liquid, miscible with water, to which Dumas (Ann. Ch. Pharm. xxvii. 135) gave the name formomethylal, regarding it as a definite compound. Malaguti, however (Ann. Ch. Phys. [2] lxx. 390), showed that it is a mixture of methylic formate and methylal, of variable composition and boiling point, and is resolved by boiling with potash into formic acid, methylic alcohol, and methylal.

Methylal is a limpid liquid smelling like acetic acid, of specific gravity 0·8551, boiling at 42° under a pressure of 0·761 met.; its vapour-density is 2·625. It dissolves in 3 volumes of water, and is separated therefrom by potash; soluble also in alcohol and ether. When gently heated with slightly diluted *nitric acid*, it decomposes, eliminating nitric oxide, without carbonic anhydride or carbonic oxide, and yielding a solution containing a considerable quantity of formic acid. It is likewise oxidised to formic acid by a mixture of *sulphuric acid and chromate of potassium*, and by *alcoholic potash*.—*Chlorine* acts very slowly on it, producing formic acid and trichloride of carbon:

$$C^3H^8O^2 + 6Cl^2 = CH^2O^2 + C^2Cl^6 + 6HCl.$$

METHYLAMINES AND METHYLAMMONIUMS. Organic bases homologous with the ethylamines, formed on the types NH^3 and NH^4 respectively, by the partial or total substitution of methyl for hydrogen; viz. methylamine, $N.H^2.CH^3$; dimethylamine, $N.H.(CH^3)^2$; trimethylamine, $N(CH^3)^3$ and tetramethylammonium, $N(CH^3)^4$. The methylamines, like the ethylamines, are known in the free state; but tetrethylammonium is known only in its salts, which are analogous in constitution to the ammonium salts. There are also amines and ammoniums in which the hydrogen is replaced, partly by methyl, partly by other alcohol-radicles, as ethyl, amyl, phenyl, &c., *e.g.* methyl-ethyl-amylamine, $N.CH^3.C^2H^5.C^5H^{11}$; methyl-triethyl-ammonium, $N.CH^3.(C^2H^5)^4$.



METHYLAMINE. $CH^5N = \left.\begin{matrix}H\\H\\CH^3\end{matrix}\right\}N$. *Methylammonia, Methylia.*—This base was discovered and fully examined by Wurtz in 1849 (Compt. rend. xxviii. 223 and 323; Ann. Ch. Phys. [3] xxx. 443). It is produced by reactions analogous to those which give rise to the formation of ethylamine (ii. 553); viz. 1. By the action of potash on cyanate or cyanurate of methyl (Wurtz).—2. By the action of potash on methyl-carbamide (methyl-urea) (Wurtz).—3. In the form of a salt, by the action of ammonia on various methylic ethers: thus iodide of methyl heated in a sealed tube with ammonia, yields hydriodate of methylamine or iodide of methylammonium, together with iodide of ammonium and the iodides of di-, tri-, and tetra-methylammonium (Hofmann).—4. By heating chloride or iodide of ammonium with wood-spirit in sealed tubes (Berthelot).—5. By the action of caustic alkalis on morphine and codeine (Wertheim, Ann. Ch. Pharm. lxxiii. 210), and by heating glycocine with anhydrous baryta (Cahours, ii. 903):

$$C^2H^5NO^2 + Ba^2O = Ba^2CO^3 + CH^5N.$$

6. In combination with hydrochloric acid, by the action of chlorine on theobromine (Rochleder and Hlasiwetz, Jahresb. 1850, p. 437) or on caffeine (Rochleder, *ibid.* 434).—7. By the action of nascent hydrogen on hydrocyanic acid: $CHN + H^4 = CH^5N$ (Mendius, Ann. Ch. Pharm. cxxi. 129).—9. Methylamine occurs in bone-oil

(Anderson, Jahresb. 1851, p. 476), and in small quantity among the products of the distillation of crude acetate (pyrolignate) of calcium. (C. G. Williams, *ibid.* 1853, p. 467.)

Preparation. 1. *By the action of potash on Cyanurate of Methyl.*—The cyanurate is heated with potash-ley in a flask surmounted with a worm-tube, to condense the aqueous vapours and separate the methylamine, which then passes on into a receiver containing a small quantity of pure water, which dissolves it. The decomposition of the methyl-cyanuric ether by potash-ley, which is very slow, may be accelerated by first melting the ether with solid potash mixed with a small quantity of water. The aqueous solution of methylamine in the receiver is saturated with hydrochloric acid and evaporated to dryness. (Wurtz.)

2. *By the action of Nascent Hydrogen on Hydrocyanic acid.* Mendius mixes the hydrocyanic acid with hydrochloric acid and alcohol, adds granulated zinc, and when the action is ended, distils off about half the liquid, and again subjects the distillate, which contains a considerable quantity of unaltered prussic acid, to the action of the zinc. By repeating this treatment a certain number of times, a solution is ultimately obtained containing hydrochlorate of methylamine mixed with chloride of zinc; and this solution distilled with lime or potash, yields free methylamine, which may be condensed in water and combined with hydrochloric acid as before. Debus (Chem. Soc. J. xvi. 249) effects the combination of the hydrogen with the prussic acid by means of platinum-black. A stream of hydrogen is passed through a mixture of 15 grms. cyanide of potassium, 15 grms. sulphuric acid, and 5 oz. water, contained in a retort, and then conducted successively through an empty vessel, a tube containing fused chloride of calcium, a tube containing platinum-black and immersed in a paraffin bath heated to 110°, and, finally, through a Liebig's bulb-apparatus filled with dilute hydrochloric acid. As soon as the mixture of prussic acid and hydrogen comes in contact with the platinum-black, dense white clouds of hydrochlorate of methylamine become perceptible, filling the apparatus from the platinum to the acid. The prussic acid mixture is gradually heated to the boiling point, and kept at that temperature, with a current of hydrogen continually passing through it, till the process is completed. The acid liquid in the bulbs, when evaporated on the water-bath, leaves a white residue almost wholly soluble in alcohol, and the alcoholic solution leaves on evaporation a colourless crystalline mass of hydrochlorate of methylamine. Part of the methylamine produced in this reaction unites with the hydrocyanic acid, forming cyanide of methylammonium, and this acts on the platinum in such a manner as to form a double cyanide of platinum and methylammonium (p. 997), which surrounds the particles of the platinum-black, and after a while prevents further action. If its formation could be prevented, this method would doubtless afford the readiest means of preparing methylamine.

To prepare pure methylamine, the hydrochlorate, perfectly dried, is mixed with twice its weight of quicklime, and the mixture introduced into a long tube closed at one end, in such quantity as to half fill it, the other half being filled with fragments of potassium-hydrate. From this tube a gas-delivery tube passes to the mercurial trough. On applying a gentle heat to the tube, beginning at the closed end, the gas is disengaged, and may be collected over the mercury.

Properties.—Methylamine is a colourless gas, having a strong ammoniacal odour. Like ammonia, it turns reddened litmus-paper blue; fumes strongly with hydrochloric acid; combines with its own volume of that gas, and half its volume of carbonic anhydride; is rapidly absorbed by water, and also by charcoal. It is distinguished from ammonia by taking fire when brought in contact with a lighted taper; it then burns with a livid yellowish flame, producing water, carbonic anhydride, and nitrogen, mixed, if the combustion be incomplete, with cyanogen and hydrocyanic acid. Specific gravity 1·13 at 25°, and 1·08 at 43°. When cooled a few degrees below 0°, it condenses to a very mobile liquid, which does not solidify in a mixture of solid carbonic acid and ether. (Wurtz.)

Methylamine is the most soluble in water of all known gases. Water at 25° absorbs 959 times, and at 12·5°, 1150 times its volume of the gas. The solution has the powerful odour of the gas, and is extremely caustic; it gives off the gas when boiled. It is decomposed by *iodine*, *bromine*, and *chlorine*. Iodine added to it, not in excess, forms hydriodate of methylamine which dissolves, and diniodomethylamine, $C(H^3I^2)N$, which remains undissolved:

$$3CH^5N + I^4 = C(H^3I^2)N + 2(CH^5N.HI).$$

Bromine and chlorine appear to act in a similar manner.

The action of aqueous methylamine on metallic salts is, for the most part, similar to that of ammonia. The salts of *magnesium*, *manganese*, *iron*, *bismuth*, *chromium*, *uranium*, and *tin* are precipitated by methylamino in the same manner as by ammonia. With *zinc-salts* methylamine forms a white precipitate, soluble in a large excess of the reagent. With *copper-salts*, a bluish-white precipitate, easily soluble in excess, and forming a deep blue solution. With *cadmium-salts*, a white precipitate, insoluble in excess. With *nickel-* and *cobalt-salts*, also, it forms precipitates insoluble in excess. These last three reactions differ from those produced by ammonia. *Acetate of lead* is scarcely clouded by methylamine, but the *nitrate* is completely precipitated. With *mercurous salts*, methylamine, like ammonia, forms a black precipitate; with *mercuric chloride*, a white, flocculent precipitate, insoluble in excess. *Nitrate of silver* is completely precipitated by methylamine; and the oxide, whether precipitated by the alkaloïd itself or by potash, dissolves readily in excess of the former. The solution, abandoned to spontaneous evaporation, deposits a black substance, which contains carbon, hydrogen, nitrogen, and silver, and is probably the analogue of fulminating silver; but does not explode either by heat or by percussion. *Chloride of silver* is also dissolved by aqueous methylamine. With *trichloride of gold*, methylamine forms a brownish-yellow precipitate, which dissolves readily in an excess of the precipitant, forming an orange-red solution. A concentrated solution of *platinic chloride* forms with methylamine a crystalline precipitate, consisting of chloroplatinate of methylamine, in the form of orange-yellow scales. The formation of this precipitate is prevented, even by slight dilution. (Wurtz.)

Decompositions.—1. Methylamine passed through a red-hot porcelain tube, filled with fragments of porcelain, is completely decomposed into free hydrogen, marsh-gas, ammonia, and hydrocyanic acid:

$$2CH^5N = NH^3.CNH + CNH + CH^4 + 3H^2.$$

If the gaseous mixture, as it issues from the tube, be passed through water, and then collected in jars over mercury, the water acquires an alkaline reaction, and is found to contain hydrocyanate of ammonia, and the gas in the jars consists, in 100 measures, of 13·77 vol. hydrocyanic acid, 71·08 hydrogen, and 14·37 marsh-gas.

2. Two vol. methylamine exploded with 4½ vol. oxygen produce 2 vol. CO^2 and 1 vol. N. Now 2 vol. CO^2 contain 2 vol. or 2 at. O, and therefore 1 at. C; and the remaining 2½ vol. O must have been consumed in burning the hydrogen, which therefore amounts to 5 vol. Hence, since the volumes of elementary gases are as the numbers of atoms contained in them, it follows that 1 molecule (= 2 vol.) of methylamine contains 1 at. carbon, 5 at. hydrogen, and 1 at. nitrogen, that is to say its formula is CH^5N. To obtain complete combustion, it is necessary to mix the gas with 3 times its volume of dry oxygen, and to add to the mixture, according to Regnault's recommendation, a certain quantity of detonating gas, derived from the electrolysis of water, also perfectly dry. (Wurtz, Ann. Ch. Phys. [3] xxx. 451.)

3. *Potassium* heated in the gas decomposes it completely, yielding free hydrogen and cyanide of potassium: $CH^5N + K = CNK + H^5$, 31·5 vol. methylamine yielding 81·5 vol. pure hydrogen, numbers which are nearly in the ratio of 2 : 5. The action, however, exhibits two stages. At first, while the heat is moderate, the volume of gas increases but little, and the residue probably contains $C(H^4K)N$, a compound analogous to amide of potassium; and this, at a higher temperature, is resolved into hydrogen and cyanide of potassium, the latter decomposition being accompanied by the considerable increase in volume which is observed. (Wurtz.)

4. With gaseous *chloride of cyanogen*, it forms hydrochlorate of methylamine, and cyanmethylamide (Cahours and Cloez, Compt. rend. xxxviii. 354)

$$2CH^5N + CNCl = CH^5N.HCl + N\left\{\begin{matrix}H\\ CH^3.\\ CN\end{matrix}\right.$$

METHYLAMINE-SALTS.—Methylamine is a strong base, neutralising acids completely, forming well-defined crystalline salts, and precipitating metallic oxides from their solutions (p. 995). Its salts, like those of ethylamine, may be regarded as compounds of methylamine with acids, or of methylammonium with the radicles of the same acids, *e. g.*:

Hydrochlorate of Methylamine. — Chloride of Methylammonium.

$$CH^5N.HCl = CH^6N.Cl.$$

Nitrate of Methylamine. — Nitrate of Methylammonium.

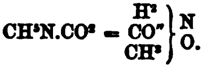
$$CH^5N.HNO^3 = CH^6N.NO^3.$$

Methylamine-salts are soluble in water, and most of them also in alcohol; the latter property affords a means of separating them from ammonium-salts, when the two occur together. They are decomposed by heating with fixed alkalis, giving off gaseous methylamine.

Bromhydrate or *Hydrobromate of Methylamine*, CH^6NBr, is obtained by the action of bromine on aqueous methylamine. It is very soluble in water and in alcohol, and crystallises from the alcoholic solution in large shining plates having an unctuous aspect and very deliquescent.

Carbonate. $(CH^6N)^2CO^3$.—This salt is prepared by distilling the fused hydrochlorate with carbonate of calcium. The product of the distillation is a very thick liquid, having a quantity of solid matter in the middle: the liquid is a highly concentrated solution of carbonate of methylamine; the solid is methyl-carbamic acid. On gently heating the contents of the receiver, the methyl-carbamic acid partly dissolves and partly volatilises. The liquid portion, as it cools, deposits crystals of the carbonate, which is highly deliquescent and volatilises even at ordinary temperatures. It is difficult, however, to obtain this salt free from methyl-carbamic acid.

Gaseous methylamine unites with its own volume of carbonic anhydride, forming methyl-carbamic acid (the so-called anhydrous carbonate of methylamine),



$$CH^5N.CO^2 = \left.\begin{matrix} H^2 \\ CO'' \\ CH^3 \end{matrix}\right\} \begin{matrix} N \\ O. \end{matrix}$$

(See CARBAMIC ACID, i. 751.)

Chlorhydrate or *Hydrochlorate of Methylamine. Chloride of Methylammonium.* $CH^6N.Cl$.—Gaseous methylamine unites with its own volume of hydrochloric acid gas, forming a white solid salt, which adheres like sal-ammoniac to the sides of the vessel.—The salt is prepared by saturating aqueous methylamine with hydrochloric acid, and evaporating to dryness. The residue dissolves easily in boiling alcohol, and crystallises on cooling in fine, large laminæ, which, at the moment of their formation, appear iridescent by reflected light. It is deliquescent; does not fuse till heated above 100°. Heated in an open vessel to a very high temperature, it volatilises in very dense vapours, which condense to a white powder on the surface of cold bodies (Wurtz). When a solution of this salt, either in water or in alcohol, is treated with amalgam of potassium, hydrogen is evolved, and the liquid becomes alkaline. Wurtz did not succeed in obtaining by this reaction an amalgam of methylammonium corresponding to the *ammoniacal amalgam* (i. 186). Neither is such a compound produced by placing mercury in a cavity in a lump of hydrochlorate of methylamine, and connecting it with the voltaic battery.

Chloro-aurate. $CH^6NCl.AuCl^3$.—On mixing a solution of hydrochlorate of methylamine with a solution of trichloride of gold, no precipitate is formed; but on evaporating till the liquid becomes very concentrated and then leaving it to cool, the double salt is obtained in splendid golden-yellow needles, soluble in water, alcohol, and ether.

Chloromercurate. $CH^6NCl.HgCl$ or $2CH^6NCl,Hhg''Cl^2$.—Formed by evaporating a mixture of 1 at. hydrochlorate of methylamine and 1 at. corrosive sublimate. The solution, when highly concentrated, yields bulky crystals of the double salt.

Chloroplatinate, $CH^6NCl.PtCl^2$ or $2CH^6NCl.PptCl^4$.—Beautiful golden-yellow scales which are insoluble in alcohol, but dissolve in boiling water and crystallise on cooling. When heated, they blacken, emitting very copious fumes and leaving a residue of platinum mixed with charcoal, which burns in the air.

For the compounds of methylamine with platinous chloride, see PLATINUM-BASES.

Sulphate.—Very soluble in water, insoluble in alcohol, uncrystallisable. When evaporated with cyanate of potassium, it yields methyl-carbamide, $N^2.H^3.CH^3.CO''$.

Cyanide of Methylammonium and Platinum, CH^6NPtCy^2.—Formed in the preparation of methylamine by passing a mixture of hydrogen and hydrocyanic acid vapour over heated platinum-black (p. 995). Part of the methylamine formed unites with the hydrocyanic acid, and the cyanide of methylammonium thus formed acts on the platinum in the manner represented by the equation—

$$CH^6NCy + HCy + Pt = CH^6NPtCy^2 + H.$$

On washing the platinum-black with water, concentrating the solution over the water-bath, and then leaving it over oil of vitriol, the double cyanide separates in long prismatic crystals having a slight brown tint. They are easily soluble in water, and leave a grey residue of platinum when strongly heated in the air. (Debus.)

Iodhydrate or *Hydriodate,* CH^6NI.—Produced, together with diniodomethylamine by the action of iodine on aqueous methylamine.

Nitrate, $CH^6N.NO^3$.—Formed by saturating aqueous methylamine with nitric acid. The solution, when evaporated, yields beautiful, right rhomboïdal prisms, very much elongated, and closely resembling the crystals of nitrate of ammonium. They are deliquescent, and dissolve very readily in water and alcohol. They are decomposed by distillation, yielding gaseous products, and drops of an oily liquid insoluble in water.

DINIODOMETHYLAMINE, $C(H^3I^2)N$. This base, formed by the action of iodine on aqueous methylamine, is a garnet-coloured powder which dissolves in alcohol, but appears to be decomposed thereby. It is decomposed by heat, but does not explode like iodide of nitrogen. It is also decomposed by potash, with formation of iodide of potassium, a volatile product having a very pungent odour, and a slight insoluble flocculent residue. (Wurtz, Ann. Ch. Phys. [3] xxx. 455.)

Dimethylamine, $C^2H^7N = N.H(CH^3)^2$. This base, isomeric with ethylamine, is produced, as a hydriodate, together with other similar compounds, by heating iodide of methyl with ammonia (Hofmann, p. 994). It is also formed by heating the so-called sulphite of aldehyde-ammonia (i. 108) in a sealed tube, or by decomposing it with lime (Petersen, Ann. Ch. Pharm. cii. 317):

$$C^2H^3(NH^4).SO^3 = C^2H^7N + SO^2 + O.$$

Gössmann, who first noticed this decomposition (*ibid.* xci. 122), supposed that the resulting base was ethylamine; but Petersen has shown that by passing the evolved gas into iodide of ethyl, and heating the liquid in a sealed tube, iodide of dimethyl-diethyl-ammonium is produced:

$$NH(CH^3)^2 + 2C^2H^5I = HI + N(CH^3)^2(C^2H^5)^2I.$$

The quantity of dimethylamine produced in this reaction is, however, very small, and Hofmann (Proc. Roy. Soc. xii. 380) finds that this base may be obtained with much greater facility by treating the mixture of the iodides of ammonium, methylammonium, &c., produced by the action of ammonia on iodide of methyl, with oxalate of ethyl, in the manner already described for the separation of the corresponding ethyl-bases (ii. 555, 558).

An alcoholic solution of ammonia gently heated with iodide of methyl in a flask provided with a condenser, solidifies into a crystalline mixture of the iodides of ammonium and of methyl-, dimethyl-, trimethyl-, and tetramethyl-ammonium. The more soluble iodides separated from the sparingly soluble iodide of tetramethylammonium are evaporated and distilled with potash; and the bases evolved, after being carefully dried by passing over hydrate of potassium, are made to pass through a powerfully refrigerated worm-tube, in which dimethylamine and trimethylamine, together with a portion of the methylamine, condense, the ammonia and the rest of the methylamine being carried off as gas and condensed in water. The mixture of the three methyl-bases is then treated with oxalate of ethyl, whereupon the methylamine immediately solidifies into a crystalline mass of dimethyloxamide, $N^2H^2(C^2O^2)''(CH^3)^2$, and the dimethylamine is converted into dimethyloxamate of ethyl, $\left.\begin{matrix}(CH^3)^2\\(C^2O^2)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$, a liquid boiling between 250° and 260°, while the trimethylamine remains unchanged and may be expelled by gently heating the mixture in a water-bath. The dimethyloxamate of ethyl is easily separated from the mixture by solution in cold water, and when distilled with hydrate of potassium, yields a mixture of alcohol and dimethylamine, oxalate of potassium remaining behind. The distillate evaporated with hydrochloric acid yields a crystallised residue of chloride of dimethylammonium, from which pure dimethylamine may be obtained by distillation with potash. (Hofmann.)

E. Lucius (Ann. Ch. Pharm. ciii. 105), by distilling guano with lime, obtained a small quantity of a base which he regarded as dimethylamine (from 28 lbs. guano. 0·5 grm. of a platinum-salt having the composition $C^2H^8NCl.PtCl^2$).

Dimethylamine is a highly alkaline liquid having a strong ammoniacal odour, easily soluble in water, and boiling between 8° and 9°. Its *gold-salt*, $C^2H^8NCl.AuCl^3$, and *platinum-salt*, $C^2H^8NCl.PtCl^2$, both crystallise well, the latter in long splendid needles, shooting through the liquid from one side of the vessel to the other. (Hofmann).

Trimethylamine, $C^3H^9N = (CH^3)^3N$. Discovered by Hofmann (Chem. Soc. Qu. J. iv. 304). Produced, together with other methyl-bases, in combination with hydriodic acid, by the action of ammonia on iodide of methyl, and separated by treatment with oxalic ether and subsequent distillation, as described under DIMETHYLAMINE. It occurs ready formed in many organic substances, especially as a product of decomposition. Hofmann (Chem. Soc. Qu. J. v. 288) found it in herring-pickle. According to Dessaignes, it occurs in human urine (Ann. Ch. Pharm. c. 218), and in the blood of the calf, twelve hours after it has been taken from the animal, but not in the perfectly fresh blood (J. Pharm. [3] xxxii. 43; Jahresb. 1857, p. 382); in the flowers of *Cratægus oxyacantha* (Wicke, *ibid.* 1854, 478; 1862, p. 330), also of *Cratægus monogyna*, *Pyrus Aucuparia*, and *Pyrus communis* (Wittstein, *ibid.*): in the stinking goosefoot, *Chenopodium vulvaria* (Dessaignes, *ibid.* 1851, p. 479; Wittstein, Wicke); in craw-fish (Wittstein), and in ergot of rye (Walz, Jahresb. 1852, p. 552; Winckler, *ibid.* 553; Rithausen, Rép. chim. pur. 1863, p. 420). It has been found also in very small quantity in guano (Hesse, *ibid.* 1857, p. 402), in putrefying yeast, (A. Müller, *ibid.*), and in putrefying wheat-dough (Sullivan, *ibid.* 1858, p. 231). It is also produced by heating narcotine with potassium-hydrate to 260°—300° (Wertheim), or with water to 250°—260° (Reynoso), see NARCOTINE; probably also in the decomposition of codeine by potash-lime. (Anderson, Jahresb. 1850, p. 430.)

The trimethylamine obtained from several of these sources was formerly mistaken for tritylamine, $C^3H^7.H^2.N$, with which it is isomeric.

Trimethylamine is an oily alkaline liquid having a strong odour of stale fish. It boils at 9° (Hofmann), which is but little above the boiling point of dimethylamine. When a rapid succession of electric sparks from an induction-coil is passed through the vapour, it is slowly decomposed, yielding a tarry deposit; but even a long continuance of the action does not suffice to set the whole of the nitrogen free. (Hofmann and Buff, Ann. Ch. Pharm. cxiii. 129.)

It unites with acids, forming crystallisable salts. The *sulphate* mixed with *sulphate of aluminium* forms large crystals of trimethylamine-alum, probably having the composition $\left.\begin{matrix}C^3H^{10}N\\All'''\end{matrix}\right\}(SO^4)^2.12H^2O$, analogous to that of ammonia-alum; they melt at 100°, and give off their water of crystallisation with intumescence at 120°. (Reckenschuss, Ann. Ch. Pharm. lxxxiii. 343.)

Trimethylamine unites directly with iodide of methyl, forming iodide of tetramethylammonium, $(CH^3)^4NI$, and with dibromide of ethylene, yielding the compound $C^5H^{13}NBr^2 = (CH^3)^3(C^2H^4Br)NBr$. (Hofmann, see p. 1000.)

Tetramethylammonium, $C^4H^{12}N = (CH^3)^4N$. (Hofmann, Phil. Trans. 1850, p. 93; Chem. Soc. Qu. J. iv. 321.) The iodide of this base is produced: 1. By the action of iodide of methyl on trimethylamine, the two liquids immediately uniting into a crystalline mass: $(CH^3)^3N + CH^3I = (CH^3)^4NI$.—2. By the action of ammonia on iodide of methyl. Of the five iodides, H^4NI, $(H^3Me)NI$, $(H^2Me^2)NI$, $(HMe^3)NI$, and Me^4NI, produced by this reaction, the first and last are the most abundant; and when an alcoholic solution of ammonia is used, and the iodide of methyl is in excess, the action is completed in a few hours, the hot solution, as it cools, depositing crystals of iodide of tetramethylammonium, which may be purified by washing with cold water and recrystallisation from hot water.

Hydrate of Tetramethylammonium, $\left.\begin{matrix}(CH^3)^4N\\H\end{matrix}\right\}O$, is obtained by digesting oxide of silver in the aqueous solution of the iodide. On filtering to separate iodide of silver, a strongly alkaline solution is obtained, which, when evaporated in vacuo over sulphuric acid, yields a white crystalline mass, resembling hydrate of potassium, and absorbing water and carbonic acid with avidity. When heated, it intumesces strongly, and is completely volatilised, yielding a strongly alkaline distillate. According to the decomposition-products obtained with other bodies of similar decomposition—hydrate of tetrethylammonium, for example (ii. 561), it might be expected to yield trimethylamine and methylene, CH^2; but it appears to be decomposed in a different manner, as not a trace of permanent gas is given off.

Neutralised with acids, it yields crystallisable salts. The *sulphate*, *oxalate*, *nitrate*, and *hydrochlorate* have been prepared. The *nitrate* crystallises in long shining needles; the *chloroplatinate*, $(CH^3)^4NCl.PtCl^2$, in well-defined octahedrons of a deep orange-yellow colour, partially decomposed by boiling with water, like the platinum-salts of many other ammonium-bases. (Hofmann.)

Iodides of Tetramethylammonium.—Tetramethylammonium unites with iodine in several proportions. α. The *mono-iodide*, $(CH^3)^4NI$, prepared as above, crystallises in hard flat needles of dazzling whiteness; sparingly soluble in cold, more soluble in boiling water. The solution is neutral and very bitter. The crystals are nearly insoluble in alcohol, quite insoluble in ether, sparingly soluble in an alkaline liquid. (Hofmann.)

β. An alcoholic solution of iodine added to a hot solution of the mono-iodide of tetramethylammonium, forms an abundant crop of shining crystals, consisting of the *penta-iodide*, $(CH^3)^4NI^5$. This compound is decomposed by boiling with water, yielding the mono-iodide and probably iodides containing larger proportions of iodine.—γ. On adding iodine to a boiling solution of the penta-iodide in dilute alcohol, a melted mass is formed at the bottom of the liquid, which on cooling solidifies to a crystalline mass consisting of the *deca-iodide*, $(CH^3)^4NI^{10}$.—δ. A solution of the mono-iodide mixed with an alcoholic solution of iodine containing as much iodine as is required to form the tri-iodide, yields at first crystals of the penta-iodide, afterwards a mixture of the tri- and penta-iodides, which may be separated mechanically and purified by recrystallisation. The *tri-iodide*, $(CH^3)^4NI^3$, forms rhombic crystals having a deep violet colour and strong lustre; it is more soluble in alcohol than the penta-iodide. (Weltzien, Ann. Ch. Pharm. xci. 41; xcix. 1).

Iodomercurates.—α. The salt, $(CH^3)^4NI.Hhg''I^2$, is obtained in small light yellow prisms moderately soluble in alcohol: 1. by adding mercuric iodide to an excess of iodide of tetramethylammonium in hot alcoholic solution; 2. by the action of metallic mercury on the tri-iodide of tetramethylammonium, or on the following salt.

β. $2(CH^3)^4NI.3Hhg''I^2$ – This compound is obtained in fine lemon-yellow waxy scales by adding a hot alcoholic solution of iodide of tetramethylammonium to an excess of mercuric iodide, or by the action of metallic mercury on penta-iodide of tetramethylammonium. (**H. Risse**, Ann. Ch. Pharm. cvii. 223.)

Chloriodides.—A *tetrachloriodide*, $(CH^3)^4NICl^4$, analogous to Filhol's chloriodide of ammonium, NH^4ICl^4, is obtained by heating the tri- or penta-iodide with oxide of silver; iodide of silver is then immediately formed (together with iodate), and a colourless strongly alkaline solution is formed, containing hydrate and iodate of tetramethylammonium:

$$3(CH^3)^4NI^3 + 4Ag^2O + H^2O = (CH^3)^4NIO^3 + 2((CH^3)^4N.H.O) + 8AgI;$$

and on gently heating the filtered liquid with hydrochloric acid (best after neutralising it with iodic acid), chlorine is evolved, and tetrachloriodide of tetramethylammonium is deposited, as a very loosely coherent, lemon-yellow substance, smelling strongly of iodine:

$$\underset{\text{Iodate.}}{(CH^3)^4NIO^3} + 6HCl = \underset{\text{Chloriodide.}}{(CH^3)^4NICl^4} + 3H^2O + Cl^2.$$

The *trichloriodide*, $(CH^3)^4NICl^3$, is obtained as a lemon-yellow substance: 1. By mixing chloride of tetramethylammonium with chloride of iodine. 2. By passing chlorine into a solution of the mono-iodide; a precipitate of the penta-iodide is then formed, and afterwards a colourless solution which yields the tri-iodide by evaporation.

The *dichloriodide*, $(CH^3)^4NICl^2$, is deposited from an aqueous solution of the trichloriodide in shining yellow inodorous crystals belonging to the dimetric system. (**Weltzien**, *loc. cit.*)

Methyl-bases containing Ethyl and Amyl.

α. **Methyl-triethyl-ammonium.** $(CH^3)(C^2H^5)^3N$.—The *mono-iodide* of this base, obtained by the action of methylic iodide on triethylamine, resembles the iodide of tetrethylammonium (ii. 562); it is very soluble in water, forming a neutral very bitter solution which is decomposed by potash, the iodide being precipitated without alteration.

The iodide decomposed by moist oxide of silver, yields the *hydrate* which dries up to a crystalline mass resembling hydrate of tetrethylammonium, and forming crystalline salts with sulphuric, hydrochloric, nitric, and oxalic acids. The *chloroplatinate* is a beautiful crystalline precipitate containing $MeE^3NCl.PtCl^2$. (**Hofmann**, Chem. Soc. Qu. J. iv. 313.)

The *tri-iodide*, MeE^3NI^3, obtained in the manner described below for the corresponding compound of trimethyl-ethyl-ammonium, crystallises in bluish-violet quadratic laminæ, dark reddish-yellow by transmitted light, melting at 62°. (**R. Müller**, Ann. Ch. Pharm. cviii. 1.)

β. **Dimethyl-diethyl-ammonium.** $(CH^3)^2(C^2H^5)^2N$.—The *iodide* obtained by passing the vapour of diethylamine into iodide of ethyl, and heating the resulting liquid to 100° in a sealed tube, forms white tabular crystals easily soluble in water and in alcohol. The *chloroplatinate*, $Me^2E^2NCl.PtCl^2$, forms yellowish prisms or tablets moderately soluble in water, sparingly in alcohol and ether. (**Petersen**. Ann. Ch. Pharm. xci. 122.)

γ. **Trimethyl-ethyl-ammonium.** $(CH^3)^3(C^2H^5)N$.—The *mono-iodide* of this base is obtained by the direct union of trimethylamine with iodide of ethyl.

On adding 2 at. iodine to a warm alcoholic solution of 1 at. of this mono-iodide, and leaving the solution to cool, the *tri-iodide*, Me^3ENI^3, in very brittle, rhombic prisms, which are instantly resolved by water into the mono-iodide and the green penta-iodide: in alcoholic solution, on the other hand, these two compounds reunite and form the tri-iodide. The crystals of the latter are dark brown, or in thin splinters, brownish-yellow, and somewhat dichromatic; their surface-colour is bluish-violet; they melt at 64° without decomposition. (**R. Müller**, Ann. Ch. Pharm. cviii. 1.)

The *penta-iodide*, Me^3ENI^5, obtained by treating the mono- or tri-iodide in alcoholic solution with excess of iodine, or as above mentioned, by decomposing the tri-iodide with water, crystallises in quadratic laminæ exhibiting the combination $oP . \infty P\infty . P$ (the latter faces very subordinate). Angle $oP : P = 141° 0'$. The crystals are opaque with metallic lustre, yellowish in very thin layers when polished, yellowish-brown in thicker layers; surface colour, metallic green, becoming dark blue on exposure to the air; they melt at 68°. (**R. Müller**, *loc. cit.*)

δ. **Trimethyl-bromethyl-ammonium.** $C^5H^{13}BrN = (CH^3)^3(C^2H^4Br)N$.*—The bromide of this base, $C^5H^{13}NBr^2 = [(CH^3)^3(C^2H^4Br)N]Br$, is produced by the action of aqueous or alcoholic trimethylamine on bromide of ethylene, best in sealed tubes at 40°—50°: $C^3H^9N + C^2H^4Br^2 = C^5H^{13}NBr^2$. It is very soluble in boiling alcohol, whence it crystallises in white needles, less soluble in cold alcohol, insoluble in ether. Nitrate of silver added to the solution of this salt, throws down only half the bromine; and the filtrate freed from excess of silver by hydrochloric acid, yields with platinic chloride, sparingly soluble octahedral crystals of the *chloroplatinate*, $C^5H^{13}BrNCl.PtCl^2$. The corresponding *gold-salt*, $C^5H^{13}BrNCl.AuCl^3$, crystallises in golden-yellow needles. (Hofmann, Compt. rend. xlvii. 558.)

ε. **Trimethyl-vinyl-ammonium.** $C^5H^{12}N = (CH^3)^3(C^2H^3)N$.—The bromide, $C^5H^{13}NBr^2$, treated with oxide of silver gives up the whole of its bromine and yields a strongly alkaline liquid containing hydrate of trimethyl-vinyl-ammonium, $C^5H^{13}NO = \left.\begin{matrix}C^5H^{12}N\\H\end{matrix}\right\}O$, which, when neutralised with hydrochloric acid and strongly concentrated, yields with platinic chloride octahedral crystals of the *platinum-salt*, $C^5H^{12}NCl.PtCl^2$, and with auric chloride the *gold-salt*, $C^5H^{12}NCl.AuCl^3$.

The *bromide* of this base is also formed, together with the preceding, by the action of trimethylamine on bromide of ethylene, part of the latter splitting up into hydrobromic acid and bromide of vinyl: $C^2H^4Br^2 = HBr + C^2H^3Br$. (Hofmann, *loc. cit.*)

ζ. **Trimethyl-amyl-ammonium.** $(CH^3)^3(C^5H^{11})N$.—The only known salt of this base is the *tri-iodide*, which is obtained by heating a mixture of tri-methylamine and amylic iodide for some time to 160°, and treating the product with tincture of iodine. It crystallises in dark brown flattened rhombic prisms, exhibiting the combination: $\infty P \,.\, \infty\bar{P}\infty$ (often predominant), $\infty\breve{P}\infty \,.\, \breve{P}\infty \,.\, \tfrac{1}{2}\bar{P}\infty$. Angle $\infty P : \bar{P}\infty = 104° 28'$; $\bar{P}\infty : \breve{P}\infty$ at the principal axis = 112° 4′. The crystals exhibit trichroïsm; if they are placed upright and viewed so that the light may be transmitted at right angles to $\infty\breve{P}\infty$, the ordinary ray is dark brown or nearly black, the extraordinary ray light red-brown, the third tint being between the two. They melt at 80°, dissolve easily in alcohol, but are nearly insoluble in water. (R. Müller, *loc. cit.*)

This salt and the peroxides of the other bases above mentioned form with mercury, compounds analogous to those already described as produced by the action of mercury on the periodides of tetramethylammonium. (Müller.)

η. **Methyl-ethyl-amylamine.** $C^8H^{19}N = (CH^3)(C^2H^5)(C^5H^{11})N$.—This base is obtained by the dry distillation of hydrate of methylodiethyl-amyl-ammonium, water and ethylene gas being given off at the same time:

$$(CH^3)(C^2H^5)^2(C^5H^{11})N.H.O \;=\; (CH^3)(C^2H^5)(C^5H^{11})N + H^2O + C^2H^4.$$

It is a transparent oil, having a fragrant taste and smell, sparingly soluble in water. After drying over potash and rectification, it boils constantly at 135°. It dissolves slowly in acids. The *platinum-salt*, $C^8H^{20}NCl.PtCl^2$, which is very soluble in water, is precipitated on mixing its component salts in strong solution, or on evaporating the mixture, in orange-yellow oily globules which gradually solidify in splendid needles. (Hofmann, Chem. Soc. Qu. J. iv. 317.)

θ. **Methyl-diethyl-amyl-ammonium.** $C^{10}H^{24}N = (CH^3)(C^2H^5)^2(C^5H^{11})N$.—Obtained as an iodide by gradually adding methylic iodide to diethylamylamine contained in a tubulated retort provided with a condenser, the mixture solidifying on cooling into a hard white crystalline mass. This salt is very soluble in water, forming a very bitter solution, from which it is precipitated by potash in oily globules which solidify but slowly.—By digestion with oxide of silver, it is converted into the hydrate, $C^{10}H^{24}N.H.O$, in the form of a strongly alkaline solution which when evaporated to dryness and distilled is resolved into water, ethylene-gas, and methyl-ethyl-amylamine. The sulphate, nitrate, chloride, and chloroplatinate are crystalline. (Hofmann, Chem. Soc. Qu. J. iv. 316.)

METHYL-AMYL ANILINE. See PHENYLAMINES.

METHYL-AMYLIC ETHER. *Oxide of Methyl and Amyl*, $CH^3.C^5H^{11}.O$. See AMYL (i. 205).

METHYL-ANILINE. See PHENYLAMINES.

METHYL-ARSINES. See ARSENIC-RADICLES, ORGANIC (i. 400).

METHYLATE OF AMYL. Syn. with METHYL-AMYLIC ETHER.

METHYLATE OF ETHYL. See ETHYLATE OF METHYL, under ETHYL, OXIDE OF (ii. 542).

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* Respecting the constitution of this and similar bases, see AMMONIUM-BASES (i. 196).

METHYLATE OF ETHYLENE. $C^4H^{10}O^2 = \left.\begin{matrix}(C^2H^4)''\\(CH^3)^2\end{matrix}\right\}O^2$.—Wurtz (Ann. Ch. Pharm. cviii. 84), by distilling a mixture of methylic and ethylic alcohol with sulphuric acid and peroxide of manganese, obtained this compound mixed with methyl-ethylate of ethylene, $\left.\begin{matrix}(C^2H^4)''\\CH^3\\C^2H^5\end{matrix}\right\}O^2$. A compound having the same composition ($C^4H^{10}O^2$) has recently been obtained by Dancer (Chem. Soc. J. xvii. 222) from crude wood-spirit, and called by him dimethyl-acetal; but it is by no means certain that either this or Wurtz's compound is really a derivative of acetal (see ACETAL, i. 4). Dancer prepared his compound as follows:—Crude wood-spirit, well dried over lime, was distilled upwards for some time with a concentrated solution of caustic soda to decompose the methylic acetate present; the distillate was repeatedly treated with chloride of calcium, as long as that compound continued to take up methylic alcohol from it, then with a concentrated solution of acid sulphite of sodium, to remove the acetone, and afterwards distilled upwards, with caustic potash, to insure the complete decomposition of the remaining methylic acetate, the methylic alcohol formed by the decomposition of this ether being removed by chloride of calcium, and the remaining liquid finally purified by a few distillations on sodium. The product thus obtained had very nearly the composition of dimethylate of ethylene (53·3 per cent. carbon and 11·1 hydrogen), boiled at 63°—64°; had a specific gravity of 0·8787 at 6° C. (compared with water at 4° C.) and vapour-density, by experiment 3·165, calc. 3·114.

The liquid called *lignone* by Weidmann and Schweizer, and *xylite* by Völckel, was probably a mixture of this compound with some of the other constituents of crude wood-spirit.

METHYLATE OF POTASSIUM, CH^3KO, and **METHYLATE OF SODIUM,** CH^3NaO.—Compounds similar in properties and reactions to the ethylates of the same metals (ii. 542, 543); they are obtained by the action of potassium and sodium on methylic alcohol.

METHYL-BENZOLIC or **BENZYLENIC ETHER.** See *BENZYLENIC* ETHERS (i. 577).

METHYL-BROMOSALICYLIC ACID. See SALICYLIC ETHERS.

METHYL-BRUCINE. $C^{24}H^{28}N^2O^4 = C^{23}H^{25}(CH^3)N^2O^4$. (Stahlschmidt, Pogg. Ann. cviii. 503; Jahresb. 1859, p. 398.)—Obtained as a hydriodate, by treating brucine with iodide of methyl. The *hydriodate* crystallises from boiling water in shining laminæ containing $C^{24}H^{28}N^2O^4.HI.8H^2O$, and not further altered by treatment with iodide of methyl. By decomposing this salt with oxide of silver (or the sulphate with baryta-water) a solution of methyl-brucine is obtained, which is colourless at first, but soon decomposes, turning violet, and dark red when evaporated, giving off carbonic anhydride, and leaving a solution containing a base different from methyl-brucine. The *hydrobromate*, $C^{24}H^{28}N^2O^4.HBr.\frac{5}{4}H^2O$, is obtained by mixing the solution of the hydrochlorate with bromide of potassium, as a crystalline precipitate, easily soluble in water and alcohol, and crystallising from the latter in small shining prisms, which give off their water at 130°. The *hydrochlorate*, $C^{24}H^{28}N^2O^4.HCl.5H^2O$, obtained by neutralising the base with the acid, forms small shining crystals easily soluble in water and in alcohol. The *platinum-salt*, $C^{24}H^{28}N^2O^4.HCl.PtCl^2$, is a yellow precipitate insoluble in ether, easily soluble in alcohol and in water, and crystallising in needles from the latter. The *gold-salt*, $C^{24}H^{28}N^2O^4.HCl.AuCl^3$, is an orange-yellow precipitate, sparingly soluble in cold water. *Mercuric chloride* added to the solution of the hydrochlorate, forms a white curdy precipitate. The *neutral sulphate*, $(C^{24}H^{28}N^2O^4)^2H^2SO^4.8H^2O$, obtained by decomposing the hydriodate with sulphate of silver, forms a radio-crystalline mass, easily soluble in water and in alcohol. An *acid sulphate*, $C^{24}H^{28}N^2O^4.H^2SO^4.2H^2O$, obtained by treating the neutral salt with dilute sulphuric acid, forms indistinct crystals somewhat less soluble in water and alcohol.

Methyl-brucine does not appear to be poisonous; 10 grains of the sulphate given to a rabbit did not produce any poisonous effects.

METHYL-BUTYRAL. $C^4H^7O.CH^3$.—A compound produced, together with butyral $C^4H^7O.H$ (i. 689), ethyl-butyral $C^4H^7O.C^2H^5$, and butyrone (i. 697), by the dry distillation of butyrate of calcium. It boils at about 111°, has a specific gravity = 0·827 at 0°, and vapour-density = 3·13.—*Ethyl-butyral* boils at about 128°, has a specific gravity = 0·833 at 0°, and vapour-density = 3·58. (Friedel, Ann. Ch. Pharm. cviii. 122; Jahresb. 1858, p. 295.)

METHYL-CAMPHORIC ACID. See CAMPHORIC ACID (i. 732).

METHYL-CAMPHRENE, $C^9H^{13}(CH^3)O$.—A product obtained by the action of sodium and iodide of methyl on camphrene (i. 733). A mixture of equal parts of camphrene and benzene is treated with sodium in an atmosphere of hydrogen, till the sodium remains unaltered even on heating, and the solution is then cohobated with excess of methylic iodide. On adding water to the resulting liquid, a brown oil is thrown down, which, after repeated rectification, yields methyl-camphrene as a colourless aromatic liquid boiling between 225° and 230°. (H. Schwanert, Ann. Ch. Pharm. cxxiii. 298.)

Camphrene is an oily body produced by heating common camphor with sulphuric acid. Chautard, who discovered it, assigned to it the formula $C^9H^{12}O$; but according to Schwanert, it has the composition $C^9H^{14}O$, isomeric with phorone (*q. v.*).

METHYL-CAPRINOL. $\left.\begin{matrix}C^{10}H^{19}O\\CH^3\end{matrix}\right\}$.—This, according to Harbordt (Ann. Ch. Pharm. cxxiii. 293), is the rational constitution of the essential constituent of oil of rue, regarded by C. G. Williams as euodic aldehyde, $C^{11}H^{21}O.H$. (See Rue, Oil of.)

METHYL-CAPROYL. See Methyl-hexyl.

METHYL-CARBAMIC ACID. See Carbamic Acid (i. 751); also Methylamine (iii. 99).

METHYL-CARBAMIDES. See Carbamide (i. 754).

According to later experiments by Wurtz (Rép. Chim. pure, 1862, p. 199), dimethyl-carbamide, $\left.\begin{matrix}(CH^3)^2\\(CO)''\\H^2\end{matrix}\right\}N^2$, prepared by the action of methylamine on cyanate of methyl, melts at 102·5° and boils between 268° and 270°; the (identical) compound obtained by treating cyanate of methyl with water, melts at 99·5°, and boils between 273° and 288°.

Methyl-ethyl-carbamide, $\left.\begin{matrix}CH^3.C^2H^5\\(CO)''\\H^2\end{matrix}\right\}N^2$, melts at 52° or 53°, and boils between 266° and 268°.

METHYL-CARBONATES. See Carbonic Ethers (i. 801).

METHYL-CHLORACETOL. $C^3H^6Cl^2$.—A compound isomeric with chloride of tritylene, produced by the action of pentachloride of phosphorus on acetone (i. 27).

METHYL-CITRIC ACIDS. See Citric Ethers (i. 1001).

METHYL-CHLOROSALICYLIC ACID. See Salicylic Ethers.

METHYL-CONINE. See Conine (ii. 6).

METHYL-CYANAMIDE. $C^2H^4N^2 = (H.CH^3.Cy)N$.—Produced, together with hydrochlorate of methylamine, by the action of gaseous chloride of cyanogen on methylamine (Cloez and Cannizzaro, Ann. Ch. Pharm. lxxviii. 228):

$$2\left[\left.\begin{matrix}CH^3\\H^2\end{matrix}\right\}N\right] + CNCl = \left.\begin{matrix}CH^3\\H^3\end{matrix}\right\}NCl + \left.\begin{matrix}CN\\CH^3\\H\end{matrix}\right\}N.$$

METHYL-CYANANILINE. See Phenylamines.

METHYL-DISULPHOPHOSPHORIC ACID. See Phosphoric Ethers.

METHYL-DITHIONIC ACID. CH^4SO^2. (J. T. Hobson, Chem. Soc. Qu. J. x. 243.)—An acid produced by the action of sulphurous anhydride on zinc-methyl. The dry gas passed into an ethereal solution of zinc-methyl, kept cool to moderate the action, is rapidly and completely absorbed, and in a little while, a white crystalline substance is formed, which is the zinc-salt of methyldithionic acid, CH^3ZnSO^2. This salt may be freed from ether and the last traces of sulphurous acid by evaporation in vacuo. It may be converted into a barium-salt by treating it with excess of caustic baryta, and from this the acid may be prepared by precipitating the baryta with dilute sulphuric acid.

Methyldithionic acid is a liquid having a feebly acid taste and reddening blue litmus. It decomposes in a short time, with deposition of sulphur, even in a very dilute solution.

The *Methyldithionates* cannot be conveniently prepared by digesting the free acid with oxides or carbonates, on account of the facility with which the acid decomposes; but they may be obtained by decomposing the zinc-salt with the corresponding bases, or the barium-salt with the sulphates. Their general formula is CH^3MSO^2 for those containing monatomic metals, and $C^2H^6M''S^2O^4$ for those containing diatomic metals.

The methyldithionates are all very soluble in water, but insoluble in alcohol and ether.

The *barium-salt*, CH^3BaSO^2 or $C^2H^6BbaS^2O^4$, is prepared by treating the solution of the zinc-salt with excess of caustic baryta, filtering to separate oxide of zinc, precipitating the excess of baryta by a stream of carbonic acid, and evaporating the filtrate at the heat of the water-bath. It is a colourless, inodorous, crystalline salt, which is precipitated from its strong aqueous solution by alcohol in the form of a white granular powder. A concentrated aqueous solution left to evaporate in vacuo, deposits the salt in cubes arranged in octahedral masses. It sustains a heat of 170° without decomposition.

The *calcium-salt*, CH^3CaSO^2 or $C^2H^6Cca''S^2O^4$, prepared in a similar manner, remains as a solid uncrystallisable mass when its concentrated solution is left to evaporate in a vacuum. The *copper-salt* is obtained as a grass-green solution, which is decomposed by evaporation with deposition of sulphur. The *magnesium-salt*, $CH^3MgSO^2.\frac{1}{2}H^2O$ or $C^2H^6Mmg''S^2O^4.H^2O$, obtained by decomposing the barium-salt with sulphate of magnesium or the zinc-salt with magnesia, forms minute colourless crystals. The *nickel-salt* is obtained by double decomposition as a grass-green solution which dries up in a vacuum, with partial decomposition, to a dirty buff-coloured amorphous mass. The *silver-salt* is obtained by dissolving carbonate of silver in the free acid, but the solution decomposes and blackens when exposed to light or heated to 100°. The *zinc-salt*, CH^3ZnSO^2 or $C^2H^6Zzn''S^2O^4$, prepared as above described, separates by evaporation from a very concentrated aqueous solution in small crystals soluble at 100°, but blackening and decomposing with an offensive odour at a somewhat higher temperature.

Methyldithionate of Ethyl.—A mixture of the barium-salt with ethyl-sulphate of potassium distilled at a high temperature, yields an oily liquid together with large quantities of sulphurous anhydride. The product washed with water, dried over chloride of calcium, and redistilled in a vacuum, forms a light straw-coloured liquid slightly heavier than water and having a peculiar fishy odour. It decomposes at the high temperature required to prepare it.

Ethyltrithionic acid, $C^4H^{12}S^3O^6$, is prepared in a similar manner to methyldithionic acid, the zinc-salt being obtained by the action of sulphurous anhydride on zinc-ethyl. Its salts, which have the general formula $C^4H^{10}M^2S^3O^6$, or for diatomic metals $C^4H^{10}M''S^3O^6$, are for the most part more stable and more easily crystallisable than the methyl-dithionates. The *barium-salt* dried over oil of vitriol contains $C^4H^{10}Bba''S^3O^6.H^2O$, gives off its water at 100°, and bears a heat of 170° without decomposition. The *copper-salt*, $C^4H^{10}Cc\overset{''}{u}S^3O^6$ (at 100°), crystallises from aqueous or alcoholic solution in greenish-blue deliquescent needles. The *silver-salt* dried over oil of vitriol in vacuo, contains $C^4H^{10}Ag^2S^3O^6$. It is white, crystalline, very soluble in water, and highly deliquescent. It is not decomposed by light or by heating to 100°, but completely at a somewhat higher temperature. The *sodium-salt*, $C^4H^{10}Na^2S^3O^6.H^2O$, obtained by dissolving carbonate of sodium in the aqueous acid, separates from the alcoholic solution by evaporation in a vacuum in small ill-defined crystals.

Zinc-salts.—The salt obtained by the action of sulphurous anhydride on zinc-ethyl, is a basic salt containing $Zzn''O.2C^4H^{10}Zzn''S^3O^6.3H^2O$, the excess of zinc-oxide arising from the action of water on the undecomposed zinc-ethyl. By crystallising this salt first from alcohol, then from water, the normal zinc-salt $C^4H^{10}Zzn''S^3O^6.H^2O$, is obtained in minute, colourless, needle-shaped crystals having a peculiar odour, and somewhat bitter taste. It retains its water of crystallisation at 100°, dissolves sparingly in water either hot or cold, also in ether; is nearly insoluble in cold, but moderately soluble in boiling alcohol.

Ethyl-trithionate of ethyl, $C^4H^{10}(C^2H^5)^2S^3O^6$, prepared by distilling the crystallised barium-salt with ethyl-sulphate of potassium in an oil-bath, is a yellow oily liquid heavier than water, having an offensive odour, insoluble in water, but miscible in all proportions with alcohol. (Hobson, Chem. Soc. Qu. J. x. 55.)

METHYLENE. CH^2.—This compound, the first of the series of hydrocarbons, C^nH^{2n}, ethylene being the second, is not known with certainty in the free state. Dumas and Peligot in 1835 (Ann. Ch. Phys. lviii. 28), by passing chloride of methyl through a porcelain tube kept at a cherry-red heat, obtained a gas which they regarded as methylene. After being agitated with water till quite free from hydrochloric acid gas and undecomposed chloride of methyl, and no longer yielded hydrochloric acid when burnt, it appeared as a colourless gas, having no reaction upon vegetable colours. It burnt with a yellow flame, and 2 vol. of it exploded with excess of oxygen, consumed 3 vol. oxygen, and produced 2 vol. carbonic anhydride. Now supposing two volumes of the gas to contain CH^2, that is to say 2 vol. hydrogen, this quantity of hydrogen would consume 1 vol. O, and the remaining 2 vol. O would form 2 vol. CO^2 with the 1 at. C in the 2 vol. of the gas. The gas could not however have been quite pure, as charcoal was deposited in the tube during its formation. Perrot obtained no evidence of the formation of methylene in the decomposition of methylic chloride by heat. (See p. 987.)

Regnault doubts the existence of methylene, inasmuch as it is not obtained by treating methyl-ether, or wood-spirit, with excess of sulphuric acid. Again, Hofmann finds that it is not produced by the decomposition of hydrate of tetramethylammonium by heat, though the hydrate of tetrethylammonium, when treated in like manner, yields abundance of ethylene.

Methylene is a diatomic radicle forming ethers analogous to those of ethylene. The acetate, bromide, chloride, iodide, oxide, sulphide, and sulpho-carbonate, have been obtained, but the series is at present much less complete than that of the ethylenic ethers.

METHYLENE, ACETATE OF. $C^5H^8O^4 = \left.\begin{matrix}(CH^2)''\\(C^2H^3O)^2\end{matrix}\right\}O^2$. (Butlerow, Ann. Ch. Pharm. cxi. 242.)—This compound is produced by the action of iodide of methylene on acetate of silver:

$$CH^2I^2 + 2C^2H^3AgO^2 = 2AgI + CH^2(C^2H^3O)^2O^4.$$

An intimate mixture of the two substances in equivalent quantities, with the addition of crystallisable acetic acid, is heated to 100° for some hours; the resulting mass is distilled in an oil-bath; the distillate is rectified, the portion which distils above 150° being collected apart; this portion is saturated with lime; and the acetate of calcium is dissolved out by water. Acetate of methylene then separates as an oil, which is dried by chloride of calcium, and freed from the last traces of iodide of methylene and acetic acid, by distillation over dry acetate of silver and a small quantity of quicklime.

It is an oily liquid heavier than water, and having an aromatic taste with pungent after-taste. It dissolves in water to a certain extent without decomposition; but when inclosed in a sealed tube with a quantity of water not sufficient to dissolve it at ordinary temperatures, and heated to 100° for twenty hours, it is dissolved and completely decomposed, yielding acetic acid and a solid volatile substance which dissolves readily in water and remains as a white residue when the solution is evaporated in vacuo. Acetate of methylene boiled with aqueous alkalis (potash or baryta-water) or heated with them in sealed tubes, is decomposed, yielding an alkaline acetate, and perhaps also a small quantity of formate. Neither in this decomposition nor in that by water is any hydrate of methylene (methyl-glycol) formed.—When acetate of methylene is heated with water and oxide of lead in a sealed glass tube, acetate of lead is formed, together with oxide of methylene:

$$2\left[\left.\begin{matrix}CH^2\\(C^2H^3O)^2\end{matrix}\right\}O^2\right] + 2Pb^2O = 4C^2H^3PbO^2 + C^2H^4O^2.$$

It is also decomposed by ammonia, but neither in this case is any methylene-glycol formed. These facts seem to show that methylene-glycol has, no existence. (Butlerow.)

METHYLENE, BROMIDE OF. CH^2Br^2.—Produced by the action of bromine on the iodide. (Butlerow.)

METHYLENE, CHLORIDE OF. CH^2Cl^2.—Produced by the action of chlorine on iodide of methylene (Butlerow, Ann. Ch. Pharm. cvii. 110; cxi. 242). When chlorine gas is passed into iodide of methylene covered with water in a retort, and the retort is gently heated, a very volatile liquid passes over into the receiver, and iodine separates in the crystalline form. The oily liquid, which is chloride of methylene, is purified by heating it with chlorine and a few drops of potash-lye, drying over chloride of calcium, and rectifying.

It is a colourless liquid, heavier than water, but lighter than the iodide. It has a penetrating odour very much like that of chloroform. Does not solidify in a mixture of snow and salt. Boils at about 40°.

According to the known boiling points of the chlorides of tetrylene, tritylene, and ethylene, that of chloride of methylene should be 65° instead of 40°. Now according to Wurtz, the difference of boiling point between chloride of ethylene and the isomeric body chloride of ethylidene (ii. 599) is 25°. If then this same difference between the boiling points of chloride of methylene and chloride of methylidene, is also 25°, the latter should boil at 40°, as the compound now under consideration actually does. Hence Butlerow thinks it not improbable that this compound is really *chloride of methylidene*, and consequently that the iodide of methylene above described is also really an iodide of methylidene; but till this point is satisfactorily ascertained, it is best to designate these bodies as methylene-compounds.

Chloride of methylene, or its isomer, monochlorinated methylic chloride, $CH^2Cl.Cl$, is produced, together with chloroform ($CHCl^2.Cl$), by bringing chloride of methyl and chlorine together in sunshine, and condensing the products by refrigeration (p. 988). (Regnault, Ann. Ch. Phys. [2] lxx. 377). The compound thus obtained has, however, a much lower boiling point, viz. 30·5° (Regnault). It unites with triethylphosphine, forming a crystalline mass of chloride of chlormethyl-triethyl-phosphonium: $CH^2Cl^2 + (C^2H^5)^3P = (CH^2Cl)(C^2H^5)^3P.Cl$. (Hofmann.)

Chloride of Dinitromethylene. $C(NO^2)^2Cl^2$. (Marignac, Rev. scient. v. 375.) —This compound, which is closely related to chloropicrin, $C(NO^2)Cl^3$ (i. 922), and is commonly known by the name of *Marignac's oil*, is obtained by condensing the gaseous products of the action of chlorine on naphthalene, and purifying the product, which separates after a while from the acid liquid in the receiver, by distillation with water. It is a colourless, transparent liquid, having a specific gravity of 1·685 at 15°, a pungent odour like that of chloride of cyanogen, and producing great irritation of the eyes. It is neutral to vegetable colours. Water dissolves only traces of it, but sufficient to impart the odour. It is very soluble in alcohol and ether, very slightly soluble in hydrochloric acid. Its boiling point is above 100°, but it distils with vapour of water. Metallic mercury absorbs the vapour, producing a mixture of chlorine, carbonic anhydride, and nitric oxide. It is not acted on by aqueous potash, but alcoholic potash dissolves it easily, the odour disappearing after some time, and a crystalline salt being precipitated which is decomposed with deflagration when heated.

METHYLENE, IODIDE OF. CH^2I^2. (Butlerow, Ann. Ch. Pharm. cvii. 110; cxi. 242.)—This compound is produced by the action of iodoform on ethylate of sodium; probably together with oxide of ethylene, thus:

$$CHI^3 + C^2H^5NaO = CH^2I^2 + C^2H^4O + NaI.$$

The best result is obtained when 9 at. ethylate of sodium (in not too concentrated solution), and not turned brown by exposure to the air, are gradually added to 4 at. pulverised iodoform. On adding water to the product, iodide of methylene separates as an oily liquid which must be washed with water and rectified over chloride of calcium. It is a yellowish strongly refracting liquid, of specific gravity 3·342 at + 5°; at + 2° it solidifies to a mass of broad shining crystalline laminæ.

Butlerow regards it as probable that the substance which Serullas obtained (Ann. Ch. Phys. xxv. 311), by the action of pentachloride of phosphorus on iodoform, was iodide of methylene; also the compound which Brüning produced (Ann. Ch. Pharm. civ. 187), by treating iodoform with alcoholic potash.

Iodide of methylene is not decomposed by *potassium* at ordinary temperatures, but on applying heat, an evolution of gas immediately takes place, ending with a violent explosion. *Sodium* acts in a similar manner, but the explosion is less violent. When *sodium-amalgam* containing $\frac{1}{8}$ of sodium is rubbed to powder and heated with iodide of methylene, a combustible gas is evolved, and iodide of sodium is formed, together with a blackish carbonaceous substance which glimmers away when set on fire. The gas is chiefly hydrogen, but appears to contain a small quantity of methylene; for when it is passed into bromine, after having been freed from vapours of iodide of methylene and of alcohol by passing first through alcohol and then through water, and the bromine is afterwards treated with potash, a small quantity of oil is left undissolved having an odour like that of Dutch liquid. Heated with metallic *copper* and water in sealed tubes, it yields cuprous iodide and a gaseous mixture containing carbonic anhydride, carbonic oxide, and marsh-gas, together with ethylene and some of its higher homologues, but no methylene (Butlerow, Ann. Ch. Pharm. cxx. 356). Iodide of methylene treated with *acetate of silver* is converted into acetate of methylene (Butlerow). With *triethylphosphine* it reacts similarly to the chloride. (Hofmann.)

METHYLENE, OXIDE OF. *Dioxymethylene*, $C^2H^4O^2 = \left.\begin{matrix}CH^2\\CH^2\end{matrix}\right\}O^2$. (Butlerow, Ann. Ch. Pharm. cxi. 242; cxx. 295.)—This compound, isomeric with acetic acid and methylic formate, is produced—1. By the action of oxalate of silver on iodide of methylene:

$$2C^2Ag^2O^4 + 2CH^2I^2 = C^2H^4O^2 + 4AgI + 2CO^2 + 2CO.$$

2. By the action of oxide of silver on iodide of methylene.—3. By that of lead-oxide on acetate of methylene.—4. By the dry distillation of ethyl-glycollic acid (ii. 916). (Heintz, Jahresb. 1861, p. 448.)

Preparation.—When 1 at. iodide of methylene is intimately mixed with 1 at. oxalate of silver, and heated, a violent explosive action takes place; but if the mixture be previously triturated with twice its weight of pounded glass—or better, if it be heated under a layer of rock-oil—a slow and regular decomposition takes place; gas is abundantly evolved, consisting of carbonic anhydride and corbonic oxide; and dioxymethylene sublimes in the neck of the retort, or passes over with the vapour of rock-oil into the receiver, and there condenses in a thin white layer, which adheres closely to the sides of the receiver. It is purified by pressure between paper, and washing with ether, alcohol, and water, then with alcohol and ether, in the order here mentioned, and lastly dried over oil of vitriol and sublimed in sealed tubes.

Properties.—Dioxymethylene forms translucent, hard, crystalline crusts having an indistinct crystalline structure. It is odourless at ordinary temperatures, but emits a peculiar, sharp, irritating odour when heated. Tasteless. Neutral to litmus paper. May be sublimed without previous fusion. Begins to volatilise at 100°, but is not completely vaporised till heated above 150°; at about 152° it melts, and immediately afterwards begins to boil. A lump of it quickly heated, melts and boils at the same time. Vapour-density, obs. = 2·07; calc. = 2·08. It does not dissolve in water, alcohol, or ether when merely boiled with them; but when heated with water to 100°, in a sealed tube for several hours, it dissolves completely, forming a solution which when evaporated in a vacuum, leaves a residue consisting chiefly of the unaltered oxide. This compound does not therefore behave with water like oxide of ethylene, C^2H^4O, and indeed cannot be regarded as the ether of the hypothetical methylene-glycol, inasmuch as that ether should have the composition CH^2O; but it appears rather to be the homologue of dioxyethylene, $(C^2H^4)^2O^2$ (ii. 599).

Decompositions.—1. Dioxymethylene has a great inclination to take up an additional quantity of *oxygen*, being thereby converted into carbonic anhydride and water, and sometimes partially into formic and oxalic acid. It reduces the oxides of silver and mercury when heated with them. *Nitric acid* and a mixture of *sulphuric acid* and *chromate of potassium* converts it into carbonic anhydride and water. Inclosed together with spongy platinum in a sealed tube containing oxygen, it oxidises slowly at ordinary, quickly at higher temperatures, yielding carbonic acid and water. Heated to 100° for about 10 hours in sealed tubes with water and *peroxide of lead*, it yields carbonate and formate of lead. In the preparation of this compound by the process above given, part of it appears to be oxidised by oxygen derived from the oxalate of silver: for the volume of carbonic evolved is greater than that of the carbonic oxide (they should be equal according to the above equation); and towards the end of the operation, oxalic acid sublimes in crystals: $C^2H^4O^2 + O^3 = C^2H^2O^4 + H^2O$.—2. With red *iodide of phosphorus* it yields iodide of methylene, and is at the same time partially carbonised.—3. When *ammonia*-gas is passed over pulverised oxide of methylene, heat is evolved, a watery liquid is separated, and a volatile crystalline substance is formed possessing basic properties.—4. It is decomposed by heating with *lime-water* or dilute *potash-lye*, into formate and methylenitan (p. 1008).

METHYLENE, SULPHIDES OF. (A. Husemann, Ann. Ch. Pharm. cxxvi. 293.)—*Monomethylenic sulphide*, CH^2S, is obtained by heating monosulphide of sodium with iodide of methylene, as a loose white insoluble powder. When heated to 150° it is converted into a sublimable body, consisting of *dimethylenic sulphide*, $(CH^2)^2S^2$, and probably identical with the compound which Girard (Ann. Ch. Pharm. c. 306) obtained by the action of nascent hydrogen (from zinc and hydrochloric acid) on sulphide of carbon. When obtained as above, it crystallises in long monoclinic prisms having an intolerable odour of onions, melting at a temperature above 200°, but volatilising in considerable quantity at a much lower temperature. It is sparingly soluble in most liquids, most readily in *benzene* and *sulphide of carbon*. It forms crystalline double salts with the *chlorides of mercury, gold*, and *platinum*, also with *nitrate of silver*, and unites directly with *iodine*, forming a crystalline compound, but not with *bromine*. *Fumic nitric acid* attacks it violently, giving off nitrous fumes and forming a compound which crystallises in acute rhombohedrons, and probably consists of dimethylenic oxysulphide, $\left.\begin{matrix}CH^2\\CH^2\end{matrix}\right\}S^2O^2$ (Husemann). Girard's compound resembles that just described in its behaviour with solvents (from benzene it crystallises in quadratic prisms), and in forming crystalline compounds with nitrate of silver and the chlorides of gold and platinum; it was dissolved without decomposition by hydrochloric acid, slightly also by dilute sulphuric acid; when heated with strong sulphuric acid it decomposed, with separation of sulphur. Hot nitric acid decomposed it completely, with formation of sulphuric acid, carbonic acid, and water.

METHYLENE, SULPHOCARBONATE OF. $\left.\begin{matrix}(CS''\\CH^2\end{matrix}\right\}S^2$.—Separates on gently heating an alcoholic solution of dioxymethylene with sulphocarbonate of sodium, as a yellowish-white, amorphous, inodorous powder, insoluble in water, and converted by fuming nitric acid into methylene-sulphurous acid (Hofmann and Buckton's disulphometholic acid; Liebig's methionic acid). (Husemann.)

METHYLENE-PHOSPHONIUMS. See Phosphorus-radicles, Organic.

METHYLENE-SULPHUROUS ACID. See Sulphurous Ethers.

METHYLENITAN. $C^7H^{14}O^6$. (Butlerow, Ann. Ch. Pharm. cxx. 295.)—A saccharine substance somewhat resembling mannite, produced, together with formic acid, by the action of strong bases on dioxymethylene:

$$\underset{\text{Dioxymethylene.}}{4C^2H^4O^2} = \underset{\text{Methylenitan.}}{C^7H^{14}O^6} + \underset{\text{Formic acid.}}{CH^2O^2}.$$

Dioxymethylene dissolves when boiled with excess of baryta- or lime-water, and if lime-water be gradually added to the boiling solution till it assumes a deep yellow colour, the liquid remains neutral, is no longer precipitable by carbonic acid, and when evaporated in a vacuum, yields a yellowish syrup, consisting of methylenitan, mixed with crystalline calcic formate. On treating this residue with absolute alcohol, the methylenitan dissolves, and remains, on evaporating the alcohol, as an amorphous body (containing a little lime) having a saccharine taste, and a faint odour like that of caramel. The solution has a slight acid reaction, is coloured yellow by alkalis, and decolorised again by acids; it reduces an alkaline cupric solution almost instantly when heated with it; has no rotatory power; and does not appear to ferment with yeast. When heated for several hours to 100°, with excess of butyric acid, it forms an oily bitter compound, probably $C^7H^{11}(C^4H^7O)^3O^6$, having an odour of cheese, insoluble in water, partially volatilised in a current of air at 150°, and yielding butyrate of barium when saponified by baryta-water.

METHYLENE-STANNAMYL and **METHYLENE-STANNETHYL.** See Tin-radicles, Organic.

METHYL-ETHYL-AMYLAMINE. See p. 1001.

METHYL-ETHYL-AMYLO-PHENYL-AMMONIUM.
METHYL-ETHYL-ANILINE. } See Phenylamines.

METHYL-ETHYLATE OF ETHYLENE. $\left.\begin{matrix}(C^2H^4)''\\ CH^3.C^2H^5\end{matrix}\right\}O^2$.—Obtained, together with dimethylate of ethylene (p. 1002), by distilling a mixture of methylic and ethylic alcohol with sulphuric acid and peroxide of manganese. (Wurtz.)

METHYL-ETHYL-CARBAMIDE. See Carbamides (i. 754).

METHYL-ETHYL-CONINIUM. See Conine (ii. 6).

METHYL-ETHYLIC ETHER. See Ethyl-methylic Ether (ii. 542).

METHYL-ETHYL-PHENYLAMINE. See Phenylamines.

METHYL-ETHYL-UREA. Syn. with Methyl-ethyl-carbamide.

METHYL-HEPTYLIC ETHER. Syn. with Heptyl-methylic Ether.

METHYL-HEXYL, or *Methyl-caproyl.* $C^7H^{16} = CH^3.C^6H^{13}$.—Obtained by the electrolysis of a mixture of acetate and œnanthylate of potassium, but in small quantity only, probably because œnanthylic acid is much more easily electrolysed than acetic acid. On rectifying the resulting oily liquid, the portion which distils at 85° is found to consist chiefly of methyl-hexyl, having a vapour-density of 3·426 (calc. 3·466). (Wurtz, Ann. Ch. Phys. [3] xliv. 275.)

METHYLIA. Syn. with Methylamine.

METHYLIDENE-COMPOUNDS. See p. 1006.

METHYL-IRISINE. A violet compound obtained by v. Babo, by the action of methylic sulphate on chinoline (i. 871).

METHYL-LACTIC ACID. See Lactic Ethers.

METHYL-LUTIDINE. See Lutidine (p. 738).

METHYL-MALIC ACID. See Malic Ethers (p. 799).

METHYL-MORPHINE. See Morphine.

METHYL-NICOTINE. See Nicotine.

METHYL-NITROPHENIDINE. Syn. with Nitranisidine (i. 304).

METHYL-NITROSALICYLIC ACID. See Salicylic Ethers.

METHYL-ŒNANTHYL. $C^8H^{16}O = CH^3.C^7H^{13}O$. (Städeler, J. pr. Chem. lxxii. 246.)—A compound acetone, isomeric with caprylic aldehyde, obtained by distilling a mixture of equivalent quantities of acetate and œnanthylate of sodium; also, together with heptylic or octylic alcohol, by distilling ricinoleate of potassium or sodium with excess of caustic alkali (see Heptyl, Hydrate of, p. 144). It is a thin, colourless, neutral liquid of specific gravity 0·817 at 23°; boiling between 171° and 171·5°. Its smell recalls that of oil of rue; taste similar, and slightly burning. It makes grease-spots on paper; does not turn acid on exposure to the air, even in contact with platinum-black; burns with a bright yellow flame. It is insoluble in *water*, but mixes in all proportions with *alcohol* and *ether;* mixes with *sulphuric acid*, evolving heat, and is precipitated from the yellow solution by water, apparently unchanged. With *ammonia*, *potash*, *silver-oxide*, and *chromic acid*, it behaves like caprylic aldehyde (i. 745). With *pentachloride of phosphorus*, it yields chloride of octylene, $C^8H^{16}Cl^2$. (Dachauer, Ann. Ch. Pharm. cvi. 269.)

METHYL-ŒNANTHYLIC ETHER. Syn. with Heptyl-methylic Ether (iii. 149).

METHYL-OXALIC ACID. See Oxalic Ethers.

METHYL-OXAMIC ACID. See Oxamic Ethers.

METHYL-PARABANIC ACID. See Cholestrophane (i. 926).

METHYL-PARATARTARIC ACID. See Tartaric Ethers.

METHYL-PHENIDINE. Syn. with Anisidine (i. 304).

METHYL-PHENYLAMINE. See Phenylamines.

METHYL-PLUMBIDES. See Lead-radicles, Organic (iii. 503).

METHYL-PHOSPHINES and **PHOSPHONIUMS.** See Phosphorus-radicles, Organic.

METHYL-PHOSPHORIC ACID. See Phosphoric Ethers.

METHYL-PHOSPHOROUS ACID. See Phosphorous Ethers.

METHYL-PIPERIDINE. See Piperidine.

METHYL-PIPERYL-CARBAMIDE. See Carbamides (i. 757).

METHYL-SALICYLIC ACID. See Salicylic Ethers.

METHYL-SELENIC and **-SELENIOUS ACIDS.** See Selenic and Selenious Ethers.

METHYL-STANNETHYL. See Tin-radicles, Organic.

METHYL-STIBINES. See Antimony-radicles, Organic (i. 344).

METHYL-STRYCHNINE. See Strychnine.

METHYL-SULPHURIC ACID. See Sulphuric Ethers.

METHYL-SULPHOCARBONIC ACID. See Sulphocarbonic Ethers.

METHYL-SULPHOPHENIC ACID or **SULPHANISOLIC ACID.** An acid obtained by dissolving anisol in strong sulphuric acid (see i. 305).

METHYL-TARTARIC ACID. See Tartaric Ethers.

METHYL-THIOSINAMINE. See Thiosinamine.

METHYLURAMINE. $C^2H^7N^3$. (Dessaignes, Compt. rend. xxxviii. 839.)—A base produced by heating an aqueous solution of creatine or creatinine with mercupric oxide: carbonic anhydride is then evolved without a trace of ammonia; the oxide of mercury is partly reduced; and oxalate of methyluramine is obtained in crystals:

$$\underset{\text{Creatine.}}{2C^4H^9N^3O^2} + O^6 = \underset{\substack{\text{Oxalate of Methyl-}\\\text{uramine.}}}{(C^2H^7N^3)^2.C^2H^2O^4} + 2CO^2 + H^2O$$

$$\underset{\text{Creatine.}}{2C^4H^7N^3O} + O^6 = (C^2H^7N^3)^2.C^2H^2O^4 + 2CO^2.$$

If the quantity of oxide of mercury is too small, the crystals of oxalate of methyluramine are mixed with crystals of creatine; but when a sufficient quantity of mercuric oxide is used, the oxalate of methylamine is obtained in large quantity and quite free from creatine. To separate it completely, the solution must be repeatedly treated with alcohol and evaporated. It may also be produced by treating creatine with peroxide of lead and sulphuric acid; but this method does not yield so pure a product as the preceding. (Dessaignes, Compt. rend. xli. 1258.)

Methyluramine is obtained in the free state by heating the oxalate with a slight excess of pure milk of lime, and evaporating the filtrate in vacuo. It is a white solid body having a crystalline surface, due perhaps to absorption of carbonic acid; very deliquescent. Its taste is caustic and ammoniacal. Heated on platinum-foil, it volatilises completely, exhaling a strong odour of burnt creatine.

Methyluramine contains the elements of urea and of methylamine, *minus* 1 at. water (Dessaignes):

$$C^2H^7N^3 + H^2O = CH^4N^2O + CH^5N.$$

It may also be regarded as formed from 2 at. ammonia, by the replacement of 2 at. H by 1 at. cyanogen and 1 at. methyl respectively: $C^2H^7N^3 = N^2\left\{\begin{matrix}CN\\ CH^3\\ H^4\end{matrix}\right.$. (Gerhardt, *Traité*, iii. 941.)

Methyluramine heated with baryta-water is decomposed, giving off ammonia with an odour of sea-water. It eliminates ammonia from ammonical salts at ordinary temperatures. With the chlorides of barium and calcium, it forms copious precipitates, which are soluble in a large quantity of water, and in dilute acetic acid. With sulphate of aluminium and ferric chloride, it forms precipitates which redissolve in an excess of the precipitant. It precipitates the salts of lead, copper, and mercury; forms a whitish-yellow precipitate with nitrate of silver, and dissolves oxide and chloride of silver.

Methyluramine combines with acids, forming crystalline salts, which have a slight alkaline reaction, and when heated with caustic potash-solution, give off copious alkaline vapours consisting of ammonia and methylamine. The *sulphate*, *hydrochlorate*, and *nitrate* may be easily obtained by decomposing the oxalate with the corresponding calcium-salts.

The *chloroplatinate*, $C^2H^7N^3.HCl.PtCl^2$, is obtained, by mixing a concentrated solution of the hydrochlorate with platinic chloride, in splendid orange-coloured rhomboïds, which, when redissolved and recrystallised by cooling, often take the form of flat prisms, arranged in parallel groups. The salt when calcined emits an odour of trimethylamine.

The *oxalate*, prepared as above, forms flattened prisms arranged in parallel groups, containing $(C^2H^7N^3)^2.C^2H^2O^4.2H^2O$. It gives off its water of crystallisation at 100°, is very soluble in water, has a disagreeable taste, and blues reddened litmus slightly. Heated on platinum-foil, it exhales the same odour as creatine.

METHYL-UREAS. See METHYL-CARBAMIDES, under CARBAMIDES (i. 754).

METHYL-XANTHIC ACID. See XANTHIC ETHERS.

METOLUIDINE. Syn. with MELOBENZYLAMINE. See BENZYLAMINE (i. 576)

METHYSTICIN. A crystalline substance obtained from Kawa-root, the root of *Piper Methysticum* (see KAWA, p. 445).

MEZEREUM-SEEDS. M. Martius (Arch. Pharm. [2] cx. 39) obtained from 3 lbs. of mezereum-seeds (*Semen coccognidii*), between 20 and 26 oz. of a fatty vesicating oil, and about 2 drms. of a substance which crystallised from alcohol in white cauliflower-like masses.

MIARGYRITE. A sulphantimonite of silver, $Ag^2S.Sb^2S^3$ or $AgSbS^2$, found at Bräunsdorf, near Freiberg in Saxony, associated with argentiferous arsenical pyrites. It forms thick tabular, pyramidal, or short prismatic crystals belonging to the monoclinic system. Ratio of axes $a : b : c : = 0·3565 : 1 : 1·0377$. Angle of inclined axes = 81° 36′; $\infty P : \infty P = 39° 38′$; $oP : [P\infty] = 109° 9′$. The lateral planes are deeply striated. Cleavage parallel to $\infty P\infty$ and $[P\infty]$, imperfect. Hardness = 2. Specific gravity = 5·2 to 5·4. The crystals are opaque, with sub-metallic adamantine lustre and iron-black colour; thin splinters appear blood-red by transmitted light. Streak dark cherry-red. Fracture subconchoïdal. Very sectile. Contains according to H. Rose (Pogg. Ann. xv. 469), 21·95 per cent. sulphur, 39·14 antimony, 36·40 silver, 1·06 copper, and 0·62 iron (= 99·17); the formula requires 21·2 sulphur, 42·9 antimony and 35·9 silver. In an open tube it melts easily, gives off sulphurous anhydride, and yields a sublimate of antimonious oxide.

The *Hypargyrite* of Breithaupt contains, according to Plattner, 35 per cent. silver, and is probably a variety of miargyrite. (Dana, ii. 75.)

MIASCITE. A granular slaty rock consisting of orthoclase, mica, and elæolite sometimes with quartz, albite, and hornblende.

MICA. The generic name of a number of mineral species, including Muscovite, Phlogopite, and Biotite, distinguished by a more or less laminated structure, hence called *micaceous*. They are usually divided optically into uniaxial and biaxial micas, but in reality they are all biaxial, and apparently trimetric; but in some, viz. the biotites, the angle between the optic axes is small, not amounting to 5°, while in others, viz. the muscovites, it varies between 45° and 55°.

Chemically, micas may be divided into potash-micas, containing little or no magnesia, these being again subdivided into those which contain lithia, and those which are free from that alkali; and magnesia-micas, containing for the most part from 20 to 30 per cent. of magnesia. The micas which do not contain magnesia are those in which the optic angle of the axes is the largest: hence they are commonly distinguished as biaxial micas.

The micas, even of the same subdivision, present such differences in chemical composition (at least, according to the analyses that have hitherto been made of them), that it is not an easy matter to bring them under general formulæ. According to Rammelsberg, however, they may be represented, with considerable approach to accuracy, as follows, M denoting a mon-atomic, and R a sesqui-atomic metal:

Potash-mica . . . . . $2M^2O.3SiO^2 + n(2R^4O^3.3SiO^2)$
Magnesia-mica . . . . $2M^2O.SiO^2 + n(2R^4O^3.3SiO^2)$

According to these formulæ, the magnesia micas are orthosilicates, both terms of the second formula being reducible to the form M^4SiO^4, whereas, in the formula of the potash-micas, only the second term can be thus reduced, the first containing 2 at. silica in addition.

I. POTASH-MICA.

a. *Not containing Lithia.*

Muscovite. *Common, Oblique* or *Biaxial Mica. Muscovy glass. Verre de Muscovie. Glimmer,* in part.—This mineral occurs in trimetric forms, usually hemihedral, and having a monoclinic aspect. ∞P : ∞P = 120°. Cleavage basal eminent; occasionally also at right angles to two opposite sides of oP; separating in fibres. It also forms twins, often observable by internal markings or by polarised light; face of composition parallel to ∞P. Folia sometimes aggregated in stellar or plumose groups. Hardness = 2 to 2·3. Specific gravity = 2·75 to 3·1. Lustre more or less pearly. Colour white, grey, pale green, and violet-yellow, sometimes brown and dark olive-green; colours different in the axial and diametral directions. Streak uncoloured. Transparent to translucent. Thin laminæ, flexible and elastic. Very tough. Sectile. Biaxial; angle between optic axes varying from 45° to 75°.

When heated, it gives off more or less water, which exhibits with glass the reaction of hydrofluoric acid. Melts before the blowpipe more or less easily, to a grey or yellowish tumefied glass. Gives with fluxes the reactions of silica and iron (sometimes of manganese).

Analyses: a. From Litchfield in the State of Maine: white (Smith and Brush).—*b.* County of Carlow, Ireland: grey; angle of axes = 72° 18′ (Haughton).—*c.* Glendalough valley, County of Wicklow: angle of axes = 70° 4′; specific gravity = 2·793 (Haughton).—*d.* Ceux, near St. Etienne in the Vosges: greyish-white, reddish by transmitted light; specific gravity = 2·817 (Delesse).—*e.* Zsidovacz, in Hungary: white; specific gravity = 2·817 (Kussin).—*f.* Schwarzenstein, Zillerthal (chrome-mica; fuchsite): green (Schafhäutl).—*g.* Utö, Sweden: golden-yellow (H. Rose).—*h.* Ochotsk, Siberia (H Rose).

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Fluorine . . .	. .	. .	. .	. .	. .	0·35	0·53	0·28
Silica . . .	44·60	44·64	44·71	46·23	48·07	47·95	47·50	47·19
Alumina . . .	36·23	30·18	30·13	33·03	38·41	34·45	37·20	33·80
Chromic oxide . .	. .	. .	. .	. .	. .	3·95		
Ferric oxide . .	1·34	6·35	4·69	3·48	. .	1·80	3·20	4·47
Manganous oxide .	. .	. .	. .	. .	. .	. .	0·81	2·58
Magnesia . . .	0·37	0·72	0·90	2·10	. .	0·71	. .	
Lime . . .	0·50	. .	1·09	. .	. .	0·59	. .	0·13
Potash . . .	6·20	12·40	9·91	8·87	10·10	10·75	· 0	8·35
Soda	4·10	. .	1·27	1·45	. .	0·37	. .	
Water . . .	5·26	5·32	6·22	4·12	3·42	. .	2·63	4·07
	98·60	99·61	98·92	99·28	100·00	100·92	101·47	100·87

Common mica is a constituent of granite and its associate rocks, gneiss, syenite and mica-slate. It occurs also in more recent aggregate rocks; also in imbedded crystals in granular limestone, wacke, trachyte and basalt. Coarse lamellar aggregations of it often form the matrix of crystals of topaz, tourmaline, and other mineral species.

Mica is sometimes altered by the action of water, losing its elasticity and transparency, and often some portions of its alkalis and ferric oxide. *Margarodite* (p. 853) appears to be a mica thus altered; also, perhaps, *Damourite* (ii. 303); *Gilbertite*, a mineral found at Stonagwyn, near St. Just in Cornwall, containing, according to Lehunt, 45·15 per cent. silica, 40·11 alumina, 2·43 ferric oxide, 4·17 lime, 1·9 magnesia, and 4·25 water; and *Sericite* (*q. v.*).

β. Containing Lithia.

Lepidolite. Trimetric, often occurring in oblique, rhombic, and six-sided prisms of 119° to 120°; also in coarsely granular masses consisting of foliated scales. Cleavage basal, highly eminent. Hardness = 2·5 to 4. Specific gravity = 2·84 to 3. Lustre pearly. Colour rose-red, violet-grey, yellowish, whitish. Translucent. Angle of apparent optic axes = 70°—78°.

When heated, it gives off water exhibiting a strong reaction of hydrofluoric acid. Heated before the blowpipe, either alone or with a mixture of fluor spar and acid sulphate of potassium, it colours the flame red (in the latter case sometimes also green from the presence of boron, C. Gmelin). Melts easily before the blowpipe, and exhibits the reactions of iron and manganese. It is attacked with difficulty by hydrochloric and sulphuric acid; after fusion, the finely pulverised mineral gelatinises with the acid.

Analyses: *a.* From Zinnwald in the Erzgebirge (Lohmeyer); *b.* From the same locality (Rammelsberg); *c.* Altenberg in the Erzgebirge (Stein); *d.* Cornwall (Turner); *e.* Rozena in Moravia (Rammelsberg); *f.* Utö in Sweden (Turner); *g.* Chursdorf in Saxony (C. Gmelin); *h.* Juschakowa in the Ural (Rosales).

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Fluorine . . .	6·35	7·47	1·43	4·56	7·12	3·90	4·81	10·22
Chlorine . . .	0·21	. .	0·40	. .	. .	. .	. .	1·16
Silica . . .	42·97	46·52	47·01	50·82	51·70	50·91	52·25	48·92
Alumina . . .	20·59	21·81	20·35	21·33	26·76		28·34	20·30
Ferric oxide . .	14·18	4·68	14·34	10·09				
Ferrous oxide . .	. .	6·80						
Manganic oxide. .	. .	. .	. .	. .	1·29	1·20	4·06	4·67
Manganous oxide .	0·83	1·96	1·53					
Lime . . .	. .	. .	. .	. .	0·40	. .	. .	0·12
Magnesia . . .	. .	0·44	. .	. .	0·24			
Potash . . .	10·02	9·09	9·62	9·86	10·29	9·50	6·90	10·96
Soda	1·41	0·39	. .	. .	1·15	. .	. .	2·23
Lithia . . .	1·60	1·27	4·33	4·05	1·27	5·67	4·79	2·77
Water . . .	0·22	. .	1·53					
Phosphoric acid. .	. .	0·13	. .	. .	0·16			
	98·38	100·56	100·54	100·71	100·38	99·35	100·15	101·35

The lithia-micas contain a larger proportion of manganese than those in the preceding division. Rammelsberg restricts the name lepidolite to those which are free from iron.

2. Magnesia-Micas.

The micas of this division, mostly of dark green, brown or black colour, contain only about 40 per cent. silica, often a large quantity of iron, and magnesia as an essential constituent, sometimes to the amount of 30 per cent.

Potash is also present, but in comparatively small quantity. Moreover these micas almost always contain fluorine, and frequently water. Before the blowpipe they melt, for the most part with difficulty, to grey or blackish glasses; with fluxes they give a strong iron-reaction. They are attacked with difficulty by hydrochloric, but completely decomposed by sulphuric acid, the silica remaining in the form of the laminæ with white colour and mother-of-pearl lustre.

Phlogopite. *Rhombic Mica.*—Trimetric, occurring in rhombic or hexagonal prisms, with biaxial refraction. ∞P : ∞P = 120°. Colour yellow or copper-red; also white or colourless and different shades of brown. Cleavage as in muscovite. Angle of apparent optic axes, 5° (or less) to 20°.

Analyses: *a*, *b*, *c*. From Edwards, St. Lawrence County, New York: *a.* dark yellow-brown; *b.* and *c.* colourless, with silvery lustre (Craw).—*d.* From the Vosges: in granular lime-stone: greenish; specific gravity, 2·746 (Delesse).—*e.* Jefferson County, New York: brown; fuses easily before the blowpipe to a white enamel, and colours the flame reddish (Meitzendorff).—*f.* Sala in Sweden (Svanberg).

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Fluorine . . .	4·20	trace	trace	0·22	3·30	0·62
Silica	40·14	40·36	40·3	37·54	41·30	42·64
Alumina . . .	17·36	16·45	16·08	19·80	15·35	13·05
Ferric oxide . .	trace	trace	trace	1·80	1·77	7·90
Manganous oxide . .	. .	. .	. .	0·10	. .	1·06
Magnesia . . .	28·10	29·55	30·25	30·32	28·79	25·98
Lime						
Potash . . .	10·56	7·23	6·07	7·17	9·70	6·03
Soda	0·63	4·94	4·39	1·00	0·65*	
Loss by ignition . .	. .	0·95	2·65	1·51	0·28	3·17
	100·99	99·48	99·80	100·16	101·14	100·45

* With lithia.

This kind of mica is especially characteristic of granular limestone. The phlogopites are very liable to change, losing their elasticity and becoming pearly in lustre, often with brownish spots, as if from the hydration of the oxide of iron. In some cases, an alteration to steatite has been observed.

Biotite. *Hexagonal Mica. Uniaxial Mica.*—Probably trimetric, formerly supposed to be hexagonal. Occurs usually in tabular prisms with basal cleavage, highly eminent; common also in foliated masses. Refraction biaxial; angle between the axes less than 5°. Hardness = 2·5 to 3. Specific gravity = 2·7 to 3·1. Lustre pearly, often submetallic on the terminal faces of the prism. Colours various, as in the preceding species; usually dark green, brown, or nearly black; sometimes white or colourless. Streak uncoloured. Transparent to opaque. Thin laminæ, flexible and elastic.

Analyses: a. From Lake Baikal in Siberia (H. Rose).—*b.* Vesuvius: yellowish green; crystallised (C. Bromeis).—*c.* Monroe, New York: dark green (v. Kobell).—*d.* Greenwood Furnace, near Monroe: dark green (v. Hauer).—*e.* Schwarzenstein in the Zillerthal: green (chrome-mica) (Schafhäutl).—*f.* Eifel: pinchbeck brown (Kjerulf).—*g.* From the protogyne of the Alps: dark green; specific gravity = 3·127. Difficult of fusion before the blowpipe: perfectly decomposible by hydrochloric acid (Delesse).—*h.* Abberfoss in Finland (Svanberg).

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Fluorine . . .	0·65	. .	0·50	. .	trace	. .	1·58	0·29
Silica . . .	42·01	39·75	40·00	40·21	47·68	43·10	41·22	39·44
Alumina . . .	16·05	15·99	16·16	19·09	15·15	15·05	13·92	9·27
Ferric oxide . .	4·93	8·29	7·50	7·96	5·72	25·84	26·90	37·39
Chromic oxide . .	. .	. .	. .	. .	5·90			
Manganous oxide .	. .	. .	. .	. .	1·05	. .	1·09	2·57
Magnesia . . .	25·97	24·49	21·54	21·15	11·58	10·82	4·70	3·29
Lime . . .	. .	0·87	. .	1·55	. .	0·81	2·58	0·75
Potash . . .	7·55	8·78	10·83	5·22	7·27	4·62	6·05	5·06
Soda	. .	. .	. .	0·90	1·17	0·82	1·40	
Loss by ignition .	. .	0·75	3·00	2·89	2·86	1·50	0·90	
Titanic acid . .	. .	. .	0·20	. .	. .	1·03		
Undecomposed matter	. .	0·10						
	97·16	99·02	99·73	98·97	98·38	103·59	100·34	98·06

This species is perhaps identical with the preceding; indeed no definite line of demarcation can be drawn between them. Since the percentage of iron decreases, for the most part, as the magnesia increases, part of the iron must be present as ferrous oxide. (Rammelsberg.)

Vesuvian biotite occurs in brilliant well-defined crystals; that from Greenwood Furnace, New York, in large very regular rhombic prisms, and tetrahedral pyramids.

Biotite occurs altered to rubellan and steatite; it has also been observed altered to magnetite in the Tyrol.

For further details respecting the optical properties of micas, see Dana's *Mineralogy*, ii. 217, and for a full discussion of the chemical formulæ, Rammelsberg's *Mineralchemie*, pp. 656–672.

MICA-SLATE. A rock similar in constitution to granite, but with a distinctly foliated structure.

MICHAELITE. A white, fibrous, pearly variety of opal, from the island of St. Michael in the Azores.

MICROBROMITE. A variety of bromochloride of silver. (See Silver.)

MICROCLIN. A variety of orthoclase from Arendal in Norway. Breithaupt, however, regards it as triclinic, although the angle between the principal directions of cleavage differs by only 22′ from 90°. According to Breithaupt, also, the felspar of miascite (p. 1009) consists of microclin.

MICROCOSMIC SALT. Ammonio-sodic phosphate, $(NH^4)NaHPO^4.4H^2O$, used as a flux in blowpipe experiments. (See Blowpipe, i. 624, and Phosphates.)

MICROLITE. A variety of pyrochlore from the albite vein in Chesterfield, Massachusetts. (See Pyrochlore.)

MIDDLETONITE. A fossil resin found in the coal-seams at the Middleton collieries near Leeds, and at Newcastle. It is brownish-red, of specific gravity 1·6, nearly insoluble in alcohol, ether, and oil of turpentine, and contains 86·43 per cent. carbon, 8·01 hydrogen, and 5·56 oxygen. (Johnston, Phil. Mag. [3] xii. 261.)

MIEMITE. Syn. with Dolomite.

MIESITE. Syn. with Pyromorphite.

MILK is the liquid secreted by the mammary glands of the class of animals called *Mammalia*. Its colour is generally white, often bluish-white, more rarely yellowish; it is opaque, has little or no smell, a slightly sweet taste, and in general an alkaline reaction. The specific gravity of milk varies between 1·018 and 1·045 (Scherer); the average specific gravity of human milk = 1·032 (Simon); = 1·03267 (1·02561—1·04648). (Vernois and Becquerel.)

Chemists differ as to the reaction of fresh milk. Berzelius, Peligot, and Lassaigne ascribe an acid reaction to normal milk; Simon and others, an alkaline reaction, and consider that when it is acid, that quality is due either to the milk having been allowed to stand before testing, or to disease. Moleschott, however, found that in two cases, cow's milk (stall-fed) which had just been drawn was acid. Elsässer examined 385 different specimens of human milk, some diseased, but most healthy; of these 45 were neutral, and the rest alkaline. Rattenmann, out of 272 specimens, found only two acid, and that probably owing to some extraneous cause. On the contrary, out of 94 specimens of fresh cow's milk, Rueff found 44 acid; out of 46 specimens of mare's milk, 19 acid; sheep's milk as often acid as alkaline or neutral; and the milk of carnivorous animals (dogs and cats) always acid. Dumas remarked that dog's milk coagulates by heat like turned cow's milk. Peligot found ass's milk always acid (15 cases). The reaction of the milk seems in some measure to depend upon the nature of the food. According to D'Arat and Petit, the milk of stall-fed animals is always acid, and becomes alkaline only when they are turned out to grass. Hermbstädt found milk that had remained long in the udder, acid. Fraas caused a cow to be milked six times in a day, and found the milk in each case feebly alkaline; after an interval of 24 hours, the cow was again milked, when the first portion of the milk was found to be alkaline, the last acid. Schlossberger, however, found the milk of a cow which had not been milked for 14 days, alkaline. In some experiments the milk was as often acid as alkaline, but that drawn in the morning was more often acid than evening milk.

When milk has stood for some time, a thick yellowish-white stratum, rich in fat, collects on its surface (*cream*); while the lower portion becomes bluish-white, and poorer in fat, and at the same time increases in specific gravity. If the surrounding temperature be not too low, the milk, when previously alkaline, acquires an acid reaction, but remains homogeneous for a time. It then coagulates, fresh milk more quickly than boiled, and more rapidly if the temperature be rather elevated, and the atmosphere charged with electricity. Milk is immediately coagulated by rennet. If it be rapidly evaporated, a dense white film forms on its surface.

The spontaneous coagulation of milk appears to be caused by part of the milk-sugar undergoing acid fermentation, and thus yielding lactic acid, which precipitates the casein. A solution of pure casein is not precipitated in 10 hours by rennet, and milk rendered alkaline by addition of alkali is not coagulated by rennet (Denis). Selmi, however, coagulated alkaline milk in ten minutes with rennet, and the mother-liquor was still alkaline after the precipitation of the casein. (See Casein.)

Viewed under the microscope, fresh milk appears as a clear liquid in which the so-called *milk-globules* are suspended. They vary considerably in size (diameter = between 0·0012" and 0·0018"), and rarely in fresh milk attain the diameter of 0·0038". Without the addition of reagents, they appear merely as globules of fat.

Henle first proved the existence of an external envelope; he added acetic acid to the milk, and found that the shapes of the globules were thereby distorted. Mitscherlich found that the globules were not dissolved when milk was shaken up with ether, which would have been the case if they were a simple emulsion of fat; if, however, caustic potash or carbonate of potassium, which dissolves the envelope, was previously added, the fat was then dissolved by ether. Lehmann also remarked that the surface of the globules in milk merely treated with ether, appeared less transparent, turbid, and wrinkled, as if it had been coagulated; the ether took up the fat on the addition of phosphate of sodium. Moleschott acted on the coagulum, obtained by adding alcohol to milk, with acetic acid, and extracted the fat with ether; there remained many unbroken fat envelopes in the form of little vesicles, which he was able to fill with an ethereal solution of chlorophyll; they contained no fat. From this he not only proved the existence of the fat envelopes, but concluded also that they are organised. (*Zeitschr. fr. Physiol. Heilk.* xi. p. 696–708.)

Another kind of morphological elements, the so-called *granular bodies* (*corps granuleux, Colostrumkörperchen*), occurs in the colostrum (the milk secreted during the first two or three days after parturition). They consist of irregular conglomerations of very small fat-vesicles, united by an amorphous and somewhat granular substance. Their diameter = about 0·0111" (Henle), but varies between 0·0063" and 0·0282". Their fat is much more easily dissolved by ether than that of milk-globules. They are destroyed by potash or by acetic acid; iodine-water imparts an intensely yellow colour to them; hence they consist of very small globules of fat imbedded in an albuminous substance. They are found in human milk up to the third or fourth day after child-birth, sometimes, however, as late as 20 days after. Moleschott found in the colostrum of cows, together with milk-globules, five different kinds of granular bodies and globules (*loc. cit.*).

Human colostrum is at first yellow, on the first and second day; it then becomes lighter, and on the third or fourth day becomes white. According to G. Veit, in the passage of colostrum to milk, the milk-globules (which cohere in the colostrum) lose this property, and the largest (above 0·00166" in diameter) disappear, when a richer secretion is formed, and albumin ceases to be present in the milk. The secretion of normal milk begins on the fourth day at the earliest, but generally between the sixth and tenth day.

Epithelium-cells and *mucus-globules* are of only accidental occurrence in milk.

Fibrin occurs only when the milk contains blood.

Sometimes *infusoria* or *plants* low in the scale of organisation are found in blue cow's milk, and in that of women (Vogel). T. Fuchs ascribes the blue colour of milk to an infusorium which he calls *Vibrio cyanogeneus*; Bailleul ascribes it to a *Byssus*.

ANALYSIS.—The analysis of milk is attended with considerable difficulties. It is almost impossible to obtain a perfectly dry residue by evaporation, since the casein, saturated with fat, forms crusts which are impermeable to steam, and these are often burst asunder, thereby occasioning loss. The casein is not completely precipitated by acetic acid, part remaining in solution; neither does dried casein part with all its fat to ether.

The *casein* may be approximately estimated by evaporating milk on a water-bath or in vacuo, almost to dryness, adding acetic acid, and extracting the dried residue successively with ether, alcohol, and water (Scherer and Dumas)—or one-fifth of its weight of powdered gypsum is stirred up with the milk before evaporation, whereby spirting is avoided, the casein becomes insoluble in all solvents, and the dried residue is rendered easily pulverisable. The *fat* may then be extracted by ether and alcohol. The solid residue is determined by evaporating 1 to 3 grammes of milk in vacuo, or in a water-bath, and drying the residue in an air-bath, or in vacuo at 120°. In order to determine the *ash*, the dried substance must be ignited in oxygen gas. (Haidlen.)

Sugar.—The milk for this purpose must not be acid. To determine the sugar, the liquid may be employed which is left when casein is precipitated by sulphate of magnesium or chloride of calcium, and the excess of base precipitated by potash; or the alcoholic extract obtained in Haidlen's method of estimating casein may be used. The amount of sugar is determined by Fehling's sugar-test, or by polarised light.

Baumhauer (J. pr. Chem. lxxxiv. 145; Jahresb. 1861, p. 873) evaporates the milk in paper-filters nearly filled with pure sand or pulverised quartz, previously well-washed with hydrochloric acid and ignited. The filters are first dried by exposing them to a current of air at 110°, on a stand of peculiar construction which allows the entire surface of the paper to be exposed to the action of the air; 10 c. c. of each sample of milk is then poured upon them, taking care to distribute the milk uniformly over the surface of the sand and not to wet the outer edge. The stand with the filter is then exposed in the drying chamber to a current of air heated to 60°—70°, till the escaping air no longer deposits moisture, after which the temperature is gradually raised to 105° and kept at that point for half an hour, and the filters are finally left to cool for an hour over chloride of calcium, and weighed: this determines the total amount of solid constituents in the milk. To estimate the fat, the dried filters are drenched with anhydrous ether in funnels closed at top with glass plates and having their beaks provided with spring-clamps; the ether after half an hour's digestion is allowed to run by opening the spring-clamps, this operation being twice repeated; and the filters are rinsed two or three times with ether, then dried and weighed; the loss gives the quantity of fat. The sugar and soluble salts are next dissolved out in a similar manner with warm water (about 90 c. c.), and the total quantity of matter thus removed is determined by again drying and weighing the filter. The quantity of sugar in the aqueous solution is then determined by titration with a standard cupric solution, and the difference gives the amount of soluble salts. The sum of the amounts of fat, sugar, and soluble salts, deducted from the total quantity of solid matter previously determined, gives the quantity of insoluble salts and casein (the casein is, however, slightly soluble). To determine the total quantity of inorganic constituents, a known quantity of the milk (slightly acidulated with acetic acid) is evaporated to dryness over the water-bath and the residue is concentrated.

The following are analyses of human milk at different periods after child-birth, also of the milk of different animals.

	Human milk.				
			Clemm.		
	Vernois and Becquerel. *Normal.*	Simon.[*]	4th day after delivery.	9th.	12th.
Water	889·08	883·6	879·848	885·818	905·809
Sugar	43·64	48·2	41·135	42·979	31·537
Casein and extractive matters	39·24	34·3	35·333	36·912	29·111
Butter	26·66	25·3	42·968	35·316	33·454
Salts (ash) . . .	1·38	2·3	2·095	1·691	1·939
Solid constituents . .	„	116·4	120·152	114·182	94·191
	1000·00				

			Chevallier and Henry.		
	L'Heritier.	Chevallier and Henry.	*Cow.*	*Ass.*	*Goat.*
Water	870·6	879·8	87·02	91·65	
Sugar	63·4	65·0	4·77	6·08	
Casein	9·5	15·2	4·48	1·82	
Butter	52·0	35·5	3·13	0·11	
Salts	4·5	4·5	0·60	0·34	0·52
Solid constituents . .	129·4	120·2	100·00	100·00	100·00

				Filhol and Joly.[‡] *Ewe.*		
	Chevallier and Henry. *Ewe.*	Payen. *Mare.*	Simon. *Human colostrum.*	South-down.	Merino.	Laura-gagio.
Water	85·62	89·33	828·0	82·50	78·40	76·98
Sugar	5·00	8·75	70·0	5·35	4·37	4·16
Casein	4·50	1·62	40·0	7·90	9·02	8·30
Butter	4·20	0·20	50·0	3·70	7·60	10·40
Salts	0·68	†	3·1	0·55	0·61	0·16
	100·00	10·000	172·0 (Solid constituents.)			

Ewe's milk is thus the richest of all milks; that of the goat is but little inferior to it. Human and cow's milk stand pretty close to one another, and hence the last may be easily substituted for the first; cow's milk is, however, decidedly richer in casein and sugar. The milks of the ass and mare are the poorest of all; they contain very small quantities of butter and of casein, but are proportionally richer in sugar. The milk of the carnivora differs from that of the herbivora by an almost total absence of sugar and by a greater proportion of fat.

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[*] Mean of fourteen analyses made at different periods, with the milk of the same woman.

[†] The insoluble salts were weighed with the casein, the soluble with the sugar; they amounted to about 0·4 per cent.

[‡] Kopp and Will's, Jahresb. 1858, 564.

Constituents of Milk.

Casein (see i. 810). Simon found 4·0 per cent. casein in human colostrum, and 2·15 per cent. in the milk six days after delivery. Milk varies in composition at different times of the day. In the case of two cows fed with hay, oat-straw, beet-root, oil-cake, and bean-pods, the milk obtained in the morning (4 A.M.) contained 2·56 and 2·51 per cent. casein; mid-day, 2·23 and 2·38 respectively. In another case, the milk contained, in the morning, 2·24 and 2·25; at mid-day, 2·37 and 2·36; in the evening (7 P.M.), 2·70 and 2·71 per cent. casein respectively (Struckmann and Bödeker). Heynsius found the first portion of cow's milk richer in casein than the last portions. According to Vernois and Becquerel, the amount of casein in human milk varies directly with the quantity yielded; in cow's milk, inversely as the quantity. The milk of brunettes contains about 0·3 per cent. more casein than that of blondes. Women of feeble constitution yield almost normal milk, while those of vigorous constitution yield milk poorer in casein. In *acute diseases*, out of 19 cases, the average percentage of casein was 5·040 per cent. (3·291—5·671); and in 27 cases of *chronic diseases*, 3·257 per cent. (2·521—3·989) (Vernois and Becquerel). The milk of nurses between 15 and 20 years old contains 5·574 per cent. casein and extractive matter; 20—25, 3·873 per cent.; 25—30, 3·653 per cent.; 30—35, 4·233 per cent.; 35—40, 4·207 per cent.

An albuminous substance has been met with in milk, and especially in colostrum, which is not coagulated by rennet, but is precipitated by boiling. This is supposed to be *albumin*. G. Veit remarked that the colostrum of women, up to the third day after delivery, coagulated entirely or in part on heating. It afterwards lost this property. The filtrate obtained from the acid colostrum of the cow, after adding chloride of sodium, gave no turbidity with acetic acid, but yielded a precipitate with tannin, with alcohol, and by heat; on adding ammonia and boiling, an abundant precipitate was formed, but the liquid remained unchanged when treated in the same way with acetic acid. Hence albumin must have been present (Moleschott). Vernois and Becquerel found, in the milk of the buffalo-cow and of the goat, 1·3 per cent. albumin. Heynsius found 0·5 per cent. albumin in cow's milk previously coagulated with acetic acid; it was precipitated by boiling; but if the milk was previously boiled and coagulated by acetic acid at 40° C., no turbidity was produced in the filtrate by acetic acid or by boiling. Albumin is also found in milk in inflammatory diseases of the mammary glands, and when it contains blood and pus. Nevertheless, it must be remarked that Scherer prepared a kind of casein from normal milk, which coagulated by heat; while canine milk sometimes becomes thick on heating, but returns to its previous state on cooling. (Dumas.)

Fat. The fat of human milk has not been examined qualitatively with any degree of exactness. The butter of cow's milk has however been more particularly investigated. Pure milk-fat is a colourless or very pale yellow substance, solidifying at 26·5°, whereupon the temperature rises to 32°. It is soft and sticky above 18°. Dissolves in 28·9 pts. of boiling alcohol of specific gravity 0·822. It readily becomes rancid on exposure to the air, yielding volatile fatty acids, and then decidedly reddens litmus. It may be completely saponified, and then yields, together with glycerin, margaric, oleic, capric, caprylic, caproic, and butyric acids, or instead of the two last, vaccinic acid (Lerch), or, according to Heintz, oleïc and butic ($C^{20}H^{40}O$, melting-point = 60·75° C.), stearic, palmitic, and myristic acids (Chevreul, *Sur les Corps gras*, 1822; Bromeis, Ann. Ch. Pharm. xlii. 46, &c.; Heintz, Ann. Ch. Pharm. lxxxviii. 300, 304; Pogg. Ann. xc. 137). Bromeis reckons the composition of butter according to the quantities of acid found = 68 per cent. margarin, 30 per cent. elain, and 2 per cent. peculiar butter fat; but the components of butter seem to vary considerably.

Percentage of Fat in different kinds of Milk.

Human.[*]

2·53—3·88 (Simon).
[†]4·297—3·532—3·345 (Clemm).
3·55 (Chevallier and Henry).
2·666 (0·666—5·642) (Vernois and Becquerel).

Cow.

3·80—5·10 (Simon).
3·13 (Chevallier and Henry).
3·90 (Boussingault).
4·38 (Poggiale). (Average of 10 analyses.)
8·4 (Buffalo cow.) } (Vernois and Becquerel).
3·61 (Paris cow.) } (Vernois and Becquerel).

Mare.

6·952 (Clemm).
2·44 (Vernois and Becquerel).

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[*] Four days, nine days, and twelve days after birth respectively.

[†] Schlossberger (Ann. Chem. Pharm. cviii. 64) found in the milk from the enlarged breast of a woman, the enormous amount of 28·5 per cent. fat.

Ass.

1·21 (Simon).
1·29 (Peligot).
1·85 (Vernois and Becquerel).

Ewe.

4·20 (Chevallier and Henry).
5·13 (Vernois and Becquerel).

Sow.

1·93 (H. Scheven).

Goat.

4·08 (Payen).
3·32 (Chevallier and Henry).
5·69 (Vernois and Becquerel).

Bitch.

13·3 (Simon).
7·32—12·40 (Dumas).
8·80 (Vernois and Becquerel).

Simon found 5·00 per cent. fat in human colostrum, and, as well as **Boussingault**, 2·60 per cent. in the colostrum of the cow. According to **L'Heritier**, the milk of brunettes contains 5·63—6·48 per cent. fat, while that of blondes contains only 3·55—4·05. **Vernois** and **Becquerel** found the contrary. According to them, the percentage of fat varies with age; the milk of women from 15—20 contains 3·738 per cent.; 20—25, 2·821 per cent.; 25—30, 2·348 per cent.; 30—35, 2·864 per cent.; and from 35—40, 2·233 per cent. It increases by nearly 0·3 per cent. during the period of menstruation. The percentage of butter varies inversely as the quantity of milk produced. It decreases with imperfect nutrition.

Milk contains different proportions of fat according to the time of day at which it is obtained. The milk of a cow contained in the morning 2·17 per cent.; at midday, 2·63 per cent., and in the evening, 5·42 per cent. (**Struckmann** and **Bödeker**). It has been remarked that the first portions of milk are less rich in fat than the last portions, from which it is concluded that milk deposits cream in the udder, and that the fat-globules adhere to the sides of the milk-passages in the smaller glandular canals of the udder and teats. This difference has not been observed in human milk. **Parmentier** found the first portion of cow's milk three-fourths poorer in butter than the last. According to **Vernois** and **Becquerel**, the amount of fat in human milk increases during the first two months after delivery, but decreases between the fifth and sixth, as well as between the tenth and eleventh month. The kind of food has also a considerable influence on the percentage of fat in milk. The milk of a cow fed upon ordinary food contains 3·53 per cent. fat; on sesame bran, 4·87 per cent. **Dumas** found that canine milk was on the whole richer in fat when the animal was fed with vegetable than with animal food. In disease, **Vernois** and **Becquerel** found that the percentage of fat was sometimes increased, sometimes diminished. A consumptive cow yielded 10·73 per cent. butter. In enteritis, human milk was found to contain 3·153 per cent. fat; in pleurisy, 2·77 per cent.; in colitis, 5·412 per cent.; in delirium and fever, 0·514 cent.; typhus, 0·909 per cent.

Sugar of Milk (*Lactin*):

Percentage of Sugar in different kinds of Milk.

Human.

3·2—6·24 (Simon, Clemm, Haidlen).
4·364 (2·522—5·955) (Vernois and Becquerel).

Cow.

3·4—4·3 (Simon, &c.).
4·26—4·61 (Struckmann and Bödeker).
5·28 (average; Poggiale).
3·80 (Vernois and Becquerel).

Ass.

5·05 (Vernois and Becquerel).
4·5 (Simon, &c.).

Mare.

8·7 (Simon, &c.).
3·28 (Vernois and Becquerel).

Goat.

4·4 (Simon, &c.).
3·69 (Vernois and Becquerel).

Ewe.

4·2 (Simon, &c.).
3·94 (Vernois and Becquerel).

Sow.

3·02—3·04 (Scheven).

Canine.

1·53 (Vernois and Becquerel).
2·40 (Poggiale).

The milk of brunettes contains 7·00 and 7·12 per cent. milk-sugar, that of blondes 5·85 and 6·40 per cent. (**L'Heritier**). According to Vernois and Becquerel, that of brunettes contains 4·56; blondes, 4·47. Simon found 7 per cent. milk-sugar in human colostrum; in the milk six days after birth, 6·24 per cent.; afterwards the quantity decreased. The kind of food influences the percentage of milk-sugar to a certain extent. Bensch found that it almost disappeared from canine milk when the animal was fed exclusively with meat; on substituting vegetable food, the quantity of milk-sugar increased considerably. Poggiale found in the milk of a bitch fed with meat and bread, 2·89 per cent. milk-sugar, but after the animal had been fed exclusively on meat for 21 days, only 1·82 per cent. According to the observations of Simon and of Vernois and Becquerel, rich or poor nourishment does not sensibly affect the percentage of lactin; it varies as the quantity of milk. The milk of women from 15 to 20 years old contains 3·523 per cent. milk-sugar; from 20—25, 4·472 per cent.; 25—30, 4·577 per cent.; 30—35, 3·953 per cent.; 35—40, 3·960 per cent. In the first month after birth, the quantity of sugar in the milk decreases, but it increases considerably from the eighth to the tenth month (Vernois and Becquerel). The milk of a cow yielded in the morning 4·30 per cent. sugar; at midday, 4·72 per cent.; in the evening, 4·19 (Struckmann and Bödeker). Heynsius found that the last portions of cow's milk contained less sugar than the first. According to Simon, Donné and others, the percentage of sugar does not sensibly vary in disease. According to Vernois and Becquerel, this is the case only with *chronic* diseases, whereof in 27 cases the average amount was 4·337 per cent.; in *acute* diseases, only 3·310 (19 cases).

Salts. The *soluble* salts of milk consist of chloride of sodium, chloride of potassium, alkaline phosphates, and soda and potash combined with the casein; the *insoluble*, of phosphates of calcium and magnesium, chiefly combined with casein; sulphuric acid and ammonia-salts are not contained in fresh milk. Haidlen, Scheven, and others have found a little ferric oxide in milk.

Percentage of Ash in different kinds of Milk.

Human.

0·16—0·25 (most chemists).
0·138 (0·055—0·338) (Vernois and Becquerel).

Cow.

0·55—0·85
0·66 (Vernois and Becquerel).

Bitch.

1·2—1·5
0·78 (Vernois and Becquerel).
1·63—208 (Poggiale).

Goat.

0·62 (Vernois and Becquerel).

Sow.

1·09 (Scheven).

Ass.

0·52 (Vernois and Becquerel).

Mare.

0·52 (Vernois and Becquerel).

Sheep.

0·72 (Vernois and Becquerel).

Vernois and Becquerel found in the milk of women from 15—20 years old, 0·180 per cent. ash; 20—25, 0·143; 25—30, 0·146; 30—35, 0·144; 35—40, 0·106 per cent.

The milk of a cow yielded in the morning 0·83 per cent. ash; at midday, 0·72; and in the evening 0·78 (Struckmann and Bödeker). Heynsius found slightly less ash in the last than in the first portion of cow's milk; but the soluble and insoluble salts remained in the same relations to one another. The first portions contained 0·78 per cent. salts; the last, 0·69 per cent. Vernois and Becquerel found that the percentage of salts increased both in chronic and in acute diseases (0·173 and 0·153 per cent.); in acute enteritis, 0·174 per cent.; acute pleurisy, 0·079; typhus, 0·220.

The quantity of soluble salts is generally nearly the same as if insoluble. In human milk were found 0·4—0·9 per cent. soluble salts; in cow's milk, 0·21 per cent. soluble, and 0·28 per cent. insoluble salts. According to Weber's analysis, the ash of cow's milk contains 14·18 per cent. chloride of potassium, 4·74 per cent. chloride of sodium, 23·46 per cent. potash, 6·96 per cent. soda (combined with phosphoric, sulphuric (?) and carbonic acids), 28·4 per cent. phosphoric acid, 17·34 per cent. lime, and 2·20 per cent. magnesia. Almost all the phosphoric acid is tribasic. Vernois and Becquerel found in the ash of human milk 6·9 per cent. carbonate of calcium, 70·6 per cent. phosphate of calcium, 9·8 per cent. chloride of sodium, 7·4 per cent. sulphate of sodium, and 5·3 per cent. of other salts.

Milk, at least that of the cow, contains *alkaline carbonates*. When milk is treated with acetic acid, it evolves more gas (carbonic acid) in vacuo than the same milk without acid. (Lehmann.)

The amount of *extractive matter* in milk, as well as its nature, is unknown.

Lactic acid is not supposed to exist in fresh milk. Whether the milk owes its occasionally acid reaction to lactic or butyric acid, or to acid phosphates, is uncertain.

Rees found *urea* in the milk of a woman suffering from albuminuria; also Picard, in the milk of a woman whose urine contained no albumin.

Free *gases*, especially carbonic acid, are always present in fresh milk. (Lehmann.)

Lehmann considers *albumin* to be an abnormal constituent of milk.

Marchand found *hæmatin* dissolved in the milk of a sick cow, but no blood cells.

Glucose appears to pass into the milk from the blood, but converted into lactin; iodide of potassium and free iodine pass into the milk.

Milk is coagulated by acids, alum, and various other salts; also by tannin, alcohol, and wood-spirit.

Colostrum generally forms a turbid, yellowish liquid resembling soap-suds, of sticky consistence and strongly alkaline reaction. It undergoes lactic fermentation more easily than milk, and contains more solid constituents; in the milk of cows, asses, and goats, casein is chiefly in excess; in human milk, lactin. It contains albumin to a considerable amount. Vernois and Becquerel found in human colostrum 1—5 days after delivery, 12·28 per cent. solid residue (4·54 per cent. casein, 3·58 per cent. fat, 4·01 per cent. lactin, and 0·16 per cent. salts). Simon found 16 per cent. solid residue in the colostrum of a cow, and 14 to 15 per cent. in the milk. Crusius found in the colostrum of a cow immediately after calving, 38·4 per cent. dry residue; the next day, 30·1 per cent.; the second day, 23·1 per cent.; and afterwards in the milk, 12·5 per cent.

Human milk is more bluish than cow's milk and has a sweeter taste, reacts strongly alkaline, and acidifies less easily than other milks. Specific gravity = between 1·030 and 1·034 (1·02561 and 1·04648, Vernois and Becquerel). It contains from 11 to 13 per cent. solid constituents. It is less easily and completely coagulated by rennet, the coagulum is not so gelatinous, nor so firm and solid as that of cow's milk, and it is also more digestible. Its fat contains more elain than common butter. Healthy children of both sexes discharge from the seventh to the twelfth day of their birth a white secretion from the breast (*Hexenmilch*), either alkaline or neutral, and containing milk, but no colostrum-globules. According to Guillot, this secretion has pretty much the composition of human milk.

Cow's milk has generally a pure white or yellowish-white colour. Its specific gravity varies between 1·030 and 1·039 (Simon), 1·0302 and 1·0396 (V. and B.). It contains on an average between 13 and 14 per cent. solid matter (12·29—16·5).

Mare's milk is white. Specific gravity = between 1·034 and 1·045 (1·0203, Clemm; 1·0337, V. and B.). It yields 16·2 per cent. (9·57, V. and B.) solid residue.

Ass's milk is white; sweeter than cow's milk. Specific gravity between 1·023 and 1·035 (= 1·0346, V. and B.). Contains between 9·16 and 9·53 per cent. solid matter (10·99, V. and B.). It readily turns acid, and easily undergoes alcoholic fermentation.

Goat's milk is white, of insipid sweetish taste and peculiar odour. Specific gravity about 1·036 (1·0325, V. and B.). Contains between 13·2 and 14·5 per cent. solid residue (15·51, V. and B.). On coagulation, its casein forms thick clots.

Ewe's milk is thickish, white, of agreeable taste and smell. Specific gravity = between 1·035 and 1·041. Contains 14·38 per cent. (16·77 per cent., V. and B.) solid constituents.

Sow's milk contains between 14·51 and 11·83 solid matter.

Canine milk is rather thick, and becomes thicker on warming when it does not coagulate. Specific gravity = between 1·033 and 1·036. Contains between 22·48 and 27·46 solid residue. On evaporation, the latter is converted into grape-sugar, and the solid residue absorbs much oxygen from the air. (Bensch.)

The milk of women confined for the first time, contains more water than the milk of women who have had several children. The milk of cows varies much according to the locality; that of cows in the neighbourhood of Paris contains from 3·6 to 3·7 per cent. fat; of Tyrolean, Swiss and Dutch cows, between 7·0 and 9·8 per cent. The composition of cow's milk in the first, third, fourth, fifth and sixth months is pretty much the same, varying between 12·27 and 14·20 per cent. solid matter. In the first month it contains 13·29 per cent. residue, 4·80 per cent. casein, 4·25 per cent. butter, 3·57 per cent. lactin, and 0·66 per cent. salts; in the second month, 17·32 per cent. solid residue, 5·81 per cent. casein, 7·06 per cent. butter, 3·87 per cent. lactin, and 0·57 per cent. salts; in the eighth month, 24·73 per cent. residue, 11·50 per cent. casein, 4·41 per cent. butter, 7·67 per cent. lactin, and 1·16 per cent. salts. (Vernois and Becquerel.)

The milk of a consumptive cow yielded a large quantity of cream, but did not coagulate either by rennet or on boiling. It contained 24·97 per cent. solid residue, 10·13 per cent. casein and insoluble salts, 10·73 per cent. butter, 4·09 per cent. lactin, and soluble salts.

Milk is the most indigestible of all uncoagulated albuminoïds; its solubility in the gastric juice depends upon the consistence of its coagulum. Human milk is more readily digested than cow's milk. Frerichs found that 2½ hours after he had fed a dog with milk, all had disappeared from the stomach except a few flakes, very rich in fat. Milk introduced into the stomach was instantly coagulated, and the serum was rapidly absorbed, while the coagulum formed bulky and more or less hard clots. The digestion of milk does not begin, properly speaking, until the liquid portion has been absorbed.

Thomson has shown that the percentage of fat in milk is in no way dependent upon the amount of sugar in the food.

Bensch has remarked, and his experiments have been confirmed by Poggiale, that the milk of bitches fed exclusively on meat still contained milk-sugar, showing that sugar is formed in the organism from albuminoïds.

Cow's milk contains 30 pts. unnitrogenised substances for every 10 plastic; human milk 40 pts. unnitrogenised for every 10 plastic (Liebig). Cow's milk contains 3·78 per cent. nitrogen; human milk 1·59 per cent. A cow yields in 24 hours about 5½ litres or about 6 kgr. of milk.

With respect to the generation of milk, Lehmann and others do not suppose that the constituents of milk are derived directly from the blood. Neither casein nor lactin has been detected in blood. The sugar of blood is fermentable. Fat might transude from the blood, but it is not probable that it does so; since cholesterin, which transudes with much facility, is not found in milk, and little if any butyrin is found in blood. The composition of the milk-salts also differs widely from that of the salts of blood-serum.

Tests for milk: adulterations.—Fresh milk ought not to change its appearance on boiling. Sour milk deposits clots, or partly coagulates on boiling. A simple instrument, called a lactometer, for roughly estimating the amount of cream in milk, has been constructed by Banks. It consists of a glass tube having an internal diameter of 4 centimetres, and about 17 centimetres high. A circular ring scratched on the glass indicates a capacity of two decilitres. Above this line 30 small divisions are made, each indicating $\frac{1}{100}$th of the total capacity of the vessel up to the highest division marked 0°. The vessel is filled up to 0° and allowed to stand for 24 hours; the thickness of the stratum of cream may then be read off. Another method is that of Donné. He has invented an instrument called a galactoscope, which measures the opacity of milk; the greater opacity indicating more fat-globules, and thus a greater amount of butter. It consists of a tube with a glass plate fitted at one end, and at the other a movable glass plate. The milk is introduced by means of a small funnel, and the tube is lengthened by screwing out the movable plate until the liquid no longer transmits the light of a lamp placed at a certain distance. The plate is then screwed in until the light of the lamp is rendered just visible. According to Donné, milk which removes the plate by 27°, indicates 3·527 per cent. butter; 31°, 2·89 per cent. butter. 40° to 35° of the galactoscope = 5 per cent. cream (poor milk); 35° to 30° = 5·10 per cent. cream (common milk); 30° to 25° = 10 to 15 per cent. cream (good milk); 25° to 20° = (15 to 20 per cent. cream (very rich milk); and 20° to 15° indicates an exceedingly rich milk, the last portion from the cow.

The most common adulterations of milk are the following:—Milk obtained the day before is creamed, in order to sell the cream separately; sometimes the creamed milk is mixed with fresh milk, and about half its own volume or more of water is added to the mixture. Sometimes a colouring matter, such as brown extract of chicory, caramel, &c., is added to disguise the bluish colour of milk thus adulterated. The colouring matter remains in the serum when the milk is coagulated, and may then be detected (Payen). Flour, starch, and finely-powdered chalk are also used to adulterate milk. As the chalk readily subsides, it may then be recognised by its effervescing with hydrochloric acid. The starch-granules may be readily detected under the microscope, and distinguished from the milk-globules; if a polarising apparatus be adjusted to the microscope, each of the granules will appear marked with a black cross. The addition of tincture of iodine will also indicate the presence of starch, by imparting to it the characteristic blue colour. The macerated brains of sheep and other animals are said to be sometimes added to milk. In this case, the microscope would readily detect the presence of fragments of nerve and other organised structures, which are not present in pure milk. The addition of water is not so easily detected, since if cream has been taken from the milk, its specific gravity will increase, while the addition of water again lowers it. It may however be detected by the galactoscope, if no starch or brains have been added. The milk of diseased animals is sometimes sold. It generally has a disagreeable taste and smell, as well as a slightly viscid appearance. Pus or mucus globules will be detected in it under the microscope.

According to **Baumhauer** (*loc. cit.*) all determinations of the comparative purity of milk by instruments like those above described, are very inaccurate; he gives as the result of determinations made by his own method above described (p. 1016), that all milk may be regarded as adulterated with water, which gives less than 110 grms. of solid residue per litre (or 1928 grs.—about 3 oz. troy—per quart). The minimum quantity of butter in normal cow's milk is 22 grms. per litre (or 395 grs. per quart). Milk may be regarded as creamed, when the proportion of butter is less than ⅕th of the total weight of solid matter.

Further information will be found in the following works:

Gmelin, *Handb. d. Chemie*, viii. [2] pp. 246–273; **Lehmann**, *Lehrb. d. Phys. Chem.* 1863, ii. pp. 287–301, the same translated by **G. Day**, vol. ii. pp. 332—348; **Scherer**, *Handwörterb. d. Physiol.* ii. 449–475; **Simon**, *Die Frauenmilch, &c.*, Berlin, 1838; **Vernois** and **A. Becquerel**, *Ann. d'hygiène*, April, 1853, and *Du lait chez la femme dans l'état de santé et dans l'état de maladie*, Paris, 1853; **Payen**, *Substances alimentaires*; **Bowman**, *Medical Chemistry*; Pelouze et Frémy, *Traité de Chimie Générale*, 2me. ed. Paris, 1857, p. 195. See also the several volumes of Kopp's *Jahresbericht*.

C. E. L.

MILK QUARTZ. See QUARTZ.

MILK-SUGAR. $C^{12}H^{22}\Theta^{11}$.—Called *Lactin* by Pasteur, *Lactose* by Dumas. Pasteur, on the other hand, applies the term *lactose* to a product of the decomposition of milk-sugar (see p. 1022).

This compound, the saccharine constituent of milk, was first prepared by **Fabrizio Bartholetti**, in 1619, from whey, thence called *Manna* or *Nitrum serilactis*, and afterwards, *Galacticum Bartholetti*. It has been chiefly examined by **Bouillon Lagrange** and **Vogel** (J. Phys. lxxii. 208), **Berzelius** (Ann. Chim. xcv. 67), **Bensch** (Ann. Ch. Pharm. lxi. 221), **Vohl** (*ibid.* lxx. 360), **Winckler** (Repert. Pharm. xlii. 46), **Krause** and **Städeler** (Mitth. d. naturf. Gesellsch. in Zürich, 1854, p. 473), **Lieben** (J. pr. Chem. lxviii. 407), **Pasteur** (*ibid.* lxviii. 427), **Dubrunfraut** (*ibid.* lxviii. 422), **Luboldt** (*ibid.* lxxvii. 282), and **Berthelot** (Ann. Ch. Phys. [3] liv. 82; lx. 98); see also **Gm.** xv. 217; **Gerh.** ii. 553.

Milk-sugar has been found only in the milk of mammalia; it may, however, have been confounded in some cases with glucose, the presence of which has been detected in the blood, in the liver, and in the eggs of birds. It has not yet been formed artificially from any other compound.

It is extracted by treating milk with dilute sulphuric acid, or calf's rennet, to precipitate the curd, then filtering, and evaporating the whey to the crystallising point. This product is purified by treatment with animal charcoal and repeated crystallisation; finally, according to Krause and Städeler, by repeatedly precipitating the aqueous solution with alcohol. In some localities, especially in Switzerland, milk-sugar is prepared on the large scale from the whey obtained in the fabrication of cheese.

Milk-sugar is deposited from its aqueous solution in hemihedral trimetric crystals, exhibiting the combination $\infty\breve{P}\infty \,.\, \frac{P}{4} \,.\, oP \,.\, 2\breve{P}\infty$. Angle $oP : 2\breve{P}\infty = 109° 30'$; $oP : \frac{P}{4} = 101° 41'$. Ratio of axes, $a : b : c = 0·6215 : 1 : 0·2193$ (**Schabus**). It is white, semi-transparent, hard, and grates between the teeth. The crystals, which contain $C^{12}H^{22}O^{11}.H^2O$, do not give off any water at 100°, but the whole, amounting to 5·08 per cent. (1 at. = 5·00 per cent.) at 130°, or more quickly between 140° and 150°. The anhydrous milk-sugar which remains, forms a colourless melted mass, which solidifies in the crystalline state on cooling.

Crystallised milk-sugar is slightly hygroscopic, and dissolves in 5 or 6 pts. of cold, and 2½ pts. of boiling *water*. The saturated solution produced by prolonged contact of water with excess of milk-sugar at 10°, has a density of 1·055, contains 14·55 per cent. crystallised milk-sugar, and when left to evaporate, begins to deposit crystals as soon as it attains the density of 1·063 and contains 21·64 per cent. milk-sugar. The aqueous solution turns the plane of polarisation to the right. Dextro-rotatory power for the transition-tint, $[\alpha] = 59·3°$ (**Berthelot**); 60·28° (**Biot**). According to Poggiale, 201·9 pts. of milk-sugar produce the same deviation as 164·7 pts. cane-sugar. The dextro-rotatory power of a recently prepared solution of milk-sugar is greater in the ratio of 8 : 5, than that of the same solution after standing for some time or after being heated. The rotatory power diminishes slowly at 0°, more quickly on heating, and at the boiling heat it diminishes in two minutes to 56·4° for crystallised milk-sugar. (**E. O. Erdmann**, Jahresb. 1856, p. 671.)

Milk-sugar is insoluble in *alcohol* and in *ether*, but di
vinegar, crystallising out unaltered on evaporation.

Decompositions.—1. Dry milk-sugar turns brown when he
fusing, and at 175° gives off water, and yields lactocaran
melts, and at a higher temperature yields humus-like substan
with *dilute sulphuric acid* is converted into lactose (*vid. inf.*)
appears also to be produced by prolonged boiling with wa
or *hydrochloric acid*, and *alkalis*, decompose it, especiall
mation of brown or black products.—4. Milk-sugar is easil
agents. It reduces metallic *silver* from silver-solutions (
xcviii. 132). A solution of milk-sugar mixed with potash
forming a deep blue solution which deposits cuprous oxide,
solution of *potassio-cupric tartrate*, it throws down a smaller
(about $\frac{7}{10}$), than glucose (ii. 860). Distilled with oxidising m
acid and peroxide of manganese, it yields formic acid. V
mucic, saccharic, tartaric, and a small quantity of racemic aci

Very strong nitric acid or a mixture of *nitric* and *sulphuric*
into a substitution-product called nitro-lactin, which is
solution by water, and crystallises from alcoholic solution i
ating when heated. (Reinsch; Vohl, Jahresb. 1849, p. 47
When milk-sugar is heated to 100° for some hours with *br*
formed, probably by direct addition of bromine, a brominate
decomposed by bases, yields isodiglycolethylenic or la

Milk-sugar is not brought immediately by *yeast* into the
tation; but when it is left for some time in contact with yeas
sets in. When *cheese* or *gluten* is used as the ferment, the mil
lactic acid (ii. 631; iii. 455). Alcohol is, however, always f
especially if no chalk is added to neutralise the acid as it form
formed is greater also as the solution is more dilute.

Combinations.—Milk-sugar unites with bases, but the co
much examined. It differs from glucose, in not forming a
chloride of sodium. It absorbs about 12·5 per cent. *ammo*
it again gives up on exposure to the air. It dissolves in stron
a thick liquid from which alcohol throws down white flocks
H^2O. The compound is easily decomposed by acids, even by
sugar separating from it unaltered. With *soda* a similar c
taining 8·3 per cent. soda.

Milk-sugar dissolves easily in *milk of lime*, forming a soluti
duces turbidity, and if the liquid is concentrated, throws down
taining, when washed and dried, from 11·2 to 15·7 per cent.
similar compound containing 40·1 pure baryta.

Milk-sugar gently heated with *oxide of lead*, gives off w
aqueous solution with lead-oxide, at a temperature below
dissolves, and an insoluble compound remains suspended, conta
per cent. lead-oxide. The dissolved portion evaporated in a va
soluble mass, containing 18·1 per cent. lead-oxide: ammonia
throws down an insoluble compound.

Estimation of Milk-Sugar. Milk-sugar may be estimated
Poggiale (Compt. rend. xxviii. 505) prepares the test-liquor
of cupric sulphate, 10 grms. of cream of tartar, and 30 gr
200 grms. distilled water. The filtered liquid, which has a dee
by determining the amount of pure milk-sugar required to dec
of it. To determine the quantity of sugar in milk, it is necessa
separate the fat and the casein (p. 1016). Milk-sugar may als
rotatory power.

Products of the Transformation of Milk-su

1. Lactose or Galactose, $C^6H^{12}O^6$ (Pasteur, Compt. rend.
sugar isomeric with glucose, and bearing considerable resemblan
boiling milk-sugar for several hours with 4 pts. of water and
acid, neutralising with chalk, evaporating the filtrate to a syrup,
crystallise.

Lactose crystallises more readily than grape-sugar, in nodule
scopic, limpid, rectangular prisms acuminated at the ends,—m
sided, round-edged laminæ having a pen-shaped protuberance in
rotatory power for the transition tint, [α] = 83·22° at 15°; in

solution it is stronger, [*a*] = 139 66°, but sinks to the former magnitude slowly at ordinary temperatures, instantly on boiling.

Lactose dissolves in *water*, does not combine with *chloride of sodium*, and dissolves but very sparingly in cold *alcohol*.

Lactose yields with *nitric acid* twice as much mucic acid as milk-sugar. From an alkaline solution it reduces as much *cupric oxide* as grape-sugar. It ferments in contact with *yeast*. If the fermentation be interrupted before it is complete, the liquid still contains unaltered lactose, which therefore has not undergone any division or further alteration during the fermentation. In this fermentation the same products are formed as in the fermentation of cane-sugar. (Pasteur, Ann. Ch. Phys. [3] lviii. 356.)

2. LACTOCARAMEL, $C^6H^{10}O^5$. Produced when milk-sugar is heated for some time to 180°. It is a dark brown substance, soluble in water, insoluble in alcohol, and capable of combining with the oxides of lead and copper. (Lieben, Wien. Akad. Ber. xviii. 180; Gm. xv. 227.)

3. GALLACTIC and PECTOLACTIC ACIDS. These names are given by Bödeker and Struckmann (Ann. Pharm. c. 264) to two acids produced when milk-sugar is oxidised in alkaline solution by cupric oxide. Both are syrupy, and form uncrystallisable salts, respecting the supposed composition of which, see Gm. xv. 229.

4. NITROLACTIN is best prepared by treating milk-sugar with a mixture of nitric and sulphuric acid, and precipitating with water. It crystallises from alcoholic solution in nacreous laminæ, which detonate when heated.

MILLERITE. Native sulphide of nickel. (See NICKEL.)

MILLINGTONIA. The bark of *Millingtonia hortensis* L., used in Java as a remedy against fever, contains, according to R. Hollandt (Jahresb. 1861, p. 767) —besides starch, gum, sugar, fat, wax, and an iron-greening tannin—a small quantity of a bitter substance, and certain bodies described as humic acid, to which the formulæ $C^{34}H^{28}O^{26}$ and $C^{44}H^{37}O^{26}$ are assigned.

MILOSCHIN. A compact chromiferous mineral, probably a mechanical mixture, containing, according to Kersten (Pogg. Ann. xlvii. 485), 27·50 per cent. silica, 45·01 alumina, 3·61 chromic oxide, 0·30 lime, 0·20 magnesia, and 23·30 water (= 99·92). Colour indigo-blue to celandine-green. Hardness = 2. Specific gravity = 2·13. Yields water when heated in a tube. Infusible before the blowpipe; partly dissolved by hydrochloric acid. Found at Rudniak in Servia, associated with quartz and brown iron ore.

MIMETESITE. *Mimetene. Mimetite. Green Lead-ore. Traubenblei.* Varieties: *Kampylite, Hedyphane.*—This name is applied to several minerals, isomorphous with pyromorphite, consisting either of pure arsenato-chloride of lead, or of isomorphous mixtures of this compound with the corresponding phosphato-chloride, and with the analogous calcium-compounds. The crystals are hexagonal prisms, exhibiting the combinations P . oP (*fig.* 239, ii. 739), P . ∞P . oP (*fig.* 240), ∞P . oP . 2P2 (*fig.* 241), and P : oP . ∞P . ∞P2. Length of principal axis = 0·7392. Angle P : P; (terminal) = 142° 7'; (lateral) = 80° 25'. Cleavage imperfect parallel to P and ∞P. Hardness = 3·5. Specific gravity = 7·19 to 7·35, mimetene; 5·3 to 5·5, hedyphane; 6·8 to 6·9, kampylite. Lustre resinous. Colour pale yellow passing into brown, sometimes orange-yellow (kampylite) from the presence of chromate of lead; sometimes whitish when containing much calcic phosphate (hedyphane). Streak white or nearly so. Subtransparent to subtranslucent. Sectile. Melts before the blowpipe on charcoal, but less easily than pyromorphite; exhibits a crystalline surface on cooling, and is easily reduced to lead-globules with evolution of arsenical fumes. Soluble in nitric acid and in potash.

Analysis.—*a.* From the Azulaques mine near La Blanca, Zacatecas, Mexico: yellow needle-shaped crystals on wulfenite (Bergemann, Pogg. Ann. lxxx. 401).—*b.* Phœnixville, Chester County, Pennsylvania: colourless or yellow crystals (Smith, Sill. Am. J. [2] xx. 342).—*c.* Johann-Georgenstadt: yellow crystallised (Wöhler, Pogg. Ann. iv. 161).—*d.* Caldbeck-fell, Cumberland (Breithaupt's *kampylite*) (Rammelsberg, *ibid.* xci. 316).—*e.* Horrhausen in Saxony (Dufrénoy, *Traité de Min.* iii. 46).—*f.* Cornwall (Dufrénoy, *loc. cit.*).—*g.* Preobrajansk mine, Siberia: crystals yellow within, but black on the outside, from a coating of pyrolusite (Struve, *Rammelsberg's Mineralchemie*, p. 382).—*h.* Långbanshytta, Sweden (Breithaupt's *hedyphane*): massive, greyish-white (Kersten, Schw. J. lxii. 1).—*i.* Mina Grande, near Arqueros in Chile: yellow, earthy. (Domeyko, Ann. Min. [4] xiv. 145.)

I. *Containing only Arsenic Acid.*

	Cl.	As^2O^5.	Pb^2O.		
a.	2·44	23·06	74·96	=	100·46.

II. *Containing Arsenic and Phosphoric Acids.*

	Cl.	As^2O^5.	P^2O^5.	Pb^2O.	Ca^2O.		
b.	2·39	23·17	0·14	74·58		=	100·28
c.	not determined	21·19	not determined	75·56			
d.	2·41	18·47	3·34	76·47	0·50	=	101·19
e.	2·65	22·20	0·38	74·62		=	99·85
f.	2·31	21·65	0·79	73·87		=	98·62
g.	2·38	19·58	2·44	76·14		=	100·54

III. *Containing Lime.*

	Cl.	As^2O^5.	P^2O^5.	V^2O^3.	Pb^2O.	Ca^2O.	Cu^2O.		
h.	2·66	22·78	not determined	. .	51·03	14·09			
i.	2·41	12·06	5·36	1·94	68·46	8·31	0·96	=	99·50.*

The mineral I. is a compound of chloride of lead and pure triplumbic arsenate, $PbCl.3Pb^3AsO^4$.

Those included under II., are isomorphous mixtures of true mimetesite and pyromorphite (phosphato-chloride of lead) represented by the formula $PbCl.3Pb^3(As\,;\,P)O^4$.

In the two minerals included under III., the lead is partly replaced by calcium; the composition of *h* may be nearly represented by the formula $PbCl.3\left[\left.\begin{matrix}\frac{3}{7}Pb\\ \frac{4}{7}Cu\end{matrix}\right\}^3\left\{\begin{matrix}\frac{2}{3}As\\ \frac{1}{3}P\end{matrix}\right\}O^4\right]$.

The earthy mineral from Chile appears to be hedyphane mixed with a little vanadate of lead.

MIMOSA or **ACACIA GUM.** See Gum (ii. 953).

MIMOTANNIC ACID. Syn. with Catechu-tannic Acid (i. 817).

MINDERERI SPIRITUS. Acetate of Ammonium (i. 13).

MINERAL. This term, in its widest sense, denotes any substance not formed by the processes of organic life; in its more restricted and more usual sense, it signifies any homogeneous solid or liquid inorganic body, formed by natural processes, without the concurrence of art. Minerals understood in this sense, constitute the essential part of the earth's crust. It is usual, however, to include under the same general denomination, several substances which are evidently the remains of organised beings, chiefly vegetables, which lived upon the earth in former ages, *e.g.* coal, lignite, amber, and the several varieties of fossil resins and bitumens. Such bodies should perhaps in strictness be called fossils, but they are more usually classed with minerals, and described as such in works on Mineralogy.

MINERAL ACIDS are acids of inorganic origin, either existing ready formed in natural minerals, or formed from inorganic materials by artificial processes. The term is chiefly applied to the stronger acids, sulphuric, nitric, phosphoric, hydrochloric, &c.

MINERAL ALKALI. An old name of Soda. (See Alkali, i. 115.)

MINERAL BLUE. A term sometimes applied to Prussian blue when mixed with certain white substances, such as clay, heavy spar, gypsum, &c., which give it a light blue colour.

MINERAL CAOUTCHOUC. Syn. with Elaterite (ii. 374).

MINERAL CHAMELEON. Manganate of potassium (p. 818).

MINERAL GREEN. Scheele's green. (See Green Pigments, ii. 914.)

MINERAL INDIGO. A term applied by Keller to the blue oxide of molybdenum, formed by the reducing action of tin or stannous chloride on recently precipitated molybdic acid. (See Molybdenum, p. 1036.)

MINERAL KERMES. Amorphous Trisulphide of Antimony (i. 330).

MINERAL OIL, PITCH, RESIN. (See Petroleum.)

MINERAL PURPLE. Gold-purple or Purple of Cassius (ii. 938).

MINERAL TALLOW. Syn. with Hatchettin (p. 14).

MINERAL TURPETHUM. Mercuric sulphate. (See Sulphates.)

MINERAL WATERS. See Water.

MINERAL YELLOW. A term sometimes applied to the yellow oxychlorides of lead, used as pigments (p. 556).

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* After deduction of 1·1 alumina and ferric oxide, 2 clay, and 1·12 water.

MINNETTE. An eruptive rock occurring in the Vosges, where it forms small veins chiefly in granite and syenite. It consists of mica (the characteristic constituent) varying in colour from brownish-black to greenish, and orthoclase imbedded in a felspathic ground-mass. It is usually fine-grained, often porphyroïdal, when the felspar crystals are well developed. The ground-mass frequently also contains greyish-green or dark green hornblende already far advanced in decomposition. The rock also contains quartz (in very small quantity), triclinic felspar, chlorite, calcspar, &c., often also crocidolite. A specimen from the Ballon d'Alsace, gave by analysis:

SiO^2.	Al^4O^3.	Mn^4O^3.	Fe^4O^3.	Ca^2O.	Mg^2O.	K^2O.	Na^2O.*	H^2O.	CO^2.	
56·96	12·95	0·65	7·58	4·63	6·62	4·35	2·22	1·44	1·94	= 99·34

(Delesse, Ann. Min. [5] x. 517; Jahresb. 1857, p. 705). A rock of similar constitution, from Mittershausen in the Odenwald, has been analysed by Bunsen (Jahresb. 1861, p. 1068).

MINIUM. Red oxide of lead (p. 551).

MINJAC-TANKAWAN or **TINKAWAN.** A solid vegetable fat obtained from the fruit of a tree growing in Borneo and Sumatra. The principal portion of it, insoluble in cold alcohol, consists, like cacao-fat, of stearin, palmitin and olein; a smaller portion, soluble in cold alcohol, contains free stearic acid, palmitic acid, and traces of a volatile fatty acid. (E. Ruge, Jahresb. 1862, p. 506.)

MIRABELLES. See FRUIT (ii. 714).

MIRABILITE. Syn. with Glauber salt. (See SULPHATES.)

MISENITE. Acid sulphate of potassium, $KHSO^4$, occurring in white silky fibres in a hot tufa cavern near Misene. (Scacchi, Mem. Geol. sulla Campania, 1849, p. 98.)

MISPICKEL. Fe^2AsS = $FfeAsS$, *Arsenical pyrites, Arsenopyrite, Danaite, Plinian, Fer arsénical, prismatischer Arsenikkies.*—This mineral occurs in trimetric crystals, in which the ratio of the axes $a:b:c = 0·676 : 1 : 1·189$. Angle $\infty P : \infty P$ = 68° 7′; $\frac{1}{4}\breve{P}\infty : \frac{1}{4}P\infty$ in the basal principal section = 34° 34′. Ordinary combination $\infty P . \frac{1}{4}\breve{P}\infty$. Cleavage rather distinct, parallel to ∞P. Occurs also columnar, compact granular, or impalpable. Hardness = 5·5 to 6. Specific gravity = 6 to 6·4. Lustre metallic. Colour silver-white inclining to steel-grey. Streak dark greyish-black. Fracture uneven. Brittle. Heated in a tube, it first yields a red or brown sublimate of sulphide of arsenic, then a black sublimate of metallic arsenic. On charcoal before the blowpipe, it melts to a black magnetic bead, which sometimes exhibits the reactions of cobalt as well as those of iron. According to Berthier, when heated in a closed crucible, it gives off half its sulphur, and a fourth of its arsenic. Nitric acid decomposes it, with separation of sulphur and arsenious acid; nitro-muriatic acid, with separation of sulphur alone, which may be completely dissolved by prolonged digestion.

Analyses. a. Freiberg (Behnke, Pogg. Ann. xcviii. 184).—*b.* Ehrenfriedersdorf: *Plinian* (Plattner, *ibid.* lxxvii. 127, lxxix. 430).—*c.* Reichenstein (Weidenbusch, *Rammelsberg's Mineralchemie*, p. 58).—*d.* Melchiorstollen near Jauernick in Austrian Silesia: massive (Freitag, *ibid.*).—*e.* Sala in Sweden (Behnke, *loc. cit.*).—*f.* Altenberg, near Kupferberg in Silesia: large crystals of specific gravity 6·043 (Behnke).—*g.* Rothzechau, near Landshut in Silesia: specific gravity 6·067 (Behnke).—*h.* Wettin: small twin-crystals, of specific gravity 5·365 and 5·637 (Bäntsch, Zeitschr. f. d. ges. Naturw. vii. 372):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Sulphur	20·38	20·08	19·17	21·14	18·52	20·25	19·77	22·63
Arsenic	44·83	45·46	45·94	41·91	42·05	43·78	44·02	39·86
Antimony	. .	. .	. .	. .	1·10	1·05	0·92	
Iron	34·32	34·46	33·62	36·95	37·65	34·35	34·83	37·51
	99·53	100·00	98·73	100·00	99·32	99·43	99·54	100·00

Mispickel is also found in beds at Breitenbrunn and Raschau, Andreasberg and Joachimsthal; at Tunaberg in Sweden; and at Huel-Maudlin and Unanimity in Cornwall; also at Franconia, Jackson and Haverhill in New Hampshire, and several other localities in the United States. (Dana, ii. 63.)

Danaïte (ii. 303) and *Glaucodote* (ii. 846) are varieties of mispickel in which the iron is partly replaced by cobalt, to the amount of one-sixth in the former and one-third in the latter. (Dana, ii. 62.)

MISTLETOE. *Viscum album.*—The chemical constitution of this plant has been examined by P. Reinsch (Jahresb. 1860, p. 541), who has found in it two viscous substances called viscaoutchin and viscin (*q. v.*).

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* With a little lithia; a trace of copper was also found.

Harz. (See SULPHATES.)

MITIS-GREEN. Arsenate of copper, $2Cu^2O.As^2O^5$. (See GREEN PIGMENTS, ii. 944.)

MIZZONITE. Syn. with MEIONITE (p. 865).

MOCHA STONE or *Moss Agate*. (See AGATE, i. 62.)

MODUMITE or *Skutterudite*. An arsenide of cobalt, Co^2As^3, found at Skutterud, near Modum in Norway (i. 1042).

MOHSINE. Syn. with Leucopyrite or native proto-arsenide of iron, FeAs (p. 368).

MOHSITE. Native titanate of iron. (See TITANIUM.)

MOLECULE. This term, in its strict chemical sense, denotes the smallest quantity of a compound body that can take part in any chemical reaction. Thus, as explained in the article ATOMIC WEIGHTS (i. 457–469), the molecule of water is assumed to be $H^2O = 18$ and not $HO = 9$, because, in the great majority of cases, 18 pts. by weight ($H = 1$) is the smallest quantity of water that can be taken up by, or eliminated from, any group of elements concerned in a reaction. For a similar reason, the molecule of ammonia is assumed to be $NH^3 = 17$, and not any multiple or submultiple thereof. (See Odling, Chem. Soc. Qu. J. xi. 107.)

To enter into all the considerations by which the molecular weights of bodies are determined, would be to repeat what has already been treated in some detail in other articles of this work, especially that above referred to (see also CLASSIFICATION, i. 1007). It may therefore suffice to point out in this place that, among the purely chemical considerations which enter into the determination of this point, a prominent place must be assigned to the manner in which the elements of a compound are replaced by other radicles, simple or compound. Thus, in the four typical molecules,

$$HCl, \qquad H^2O, \qquad H^3N,. \qquad H^4C,$$

the hydrogen in the first, viz. hydrochloric acid, must be either wholly replaced or not at all; whereas in water, either the half or the whole of the hydrogen may be thus replaced, but no other fraction; and in ammonia, the substitution takes place by thirds; and in marsh-gas, by fourths. Again, sulphuric acid is regarded as dibasic, and represented by H^2SO^4; phosphoric acid as tribasic, and denoted by H^3PO^4; tartaric acid as tetrabasic, by $H^4.C^4H^2O^6$, for similar reasons.

Physical considerations likewise enter largely into the determination of molecular weights. Thus, in compound gases and all compounds whose specific gravities can be determined in the state of vapour, the molecule is assumed to be so constituted that its weight is double of the specific gravity, that is to say, of the weight of a unit-volume of the vapour. This assumption cannot at present be said to rest on any physical basis; but it is found to be true in numerous cases in which the weight of the molecule can be fixed independently of it by purely chemical considerations; and hence it is extended to others in which such verification cannot be obtained. Other physical considerations which enter into the determination of molecular weights are specific heat, boiling point, isomorphism, &c. (See ATOMIC WEIGHTS, i. 466–473; HEAT, iii. 30–40 and 89–91; ISOMORPHISM, iii. 423–432.)

The term molecule, as applied to elements, must be understood in a somewhat different sense from that which it bears when applied to compounds. The smallest quantity of an elementary body that can enter into a reaction is called, not a molecule, but an atom; and the molecule of an element is the smallest quantity, or group of atoms, that can exist in the free state. Many considerations lead us to suppose that in the majority of cases, this group consists of two elementary atoms, the molecule of hydrogen, for example, being HH. (See ATOMIC WEIGHTS, i. 466; and CHEMICAL AFFINITY, i. 857.) There are also certain compound radicles, viz. the alcohol-radicles methyl, ethyl, &c., whose molecules in the free state are generally supposed to be the doubles of those by which they enter into combination; *e.g.*, free methyl $= CH^3.CH^3$; but recent investigations on the relations between these radicles and their hydrides (pp. 182, 198), have thrown considerable doubt on the existence of these particular compound molecules.

MOLYBDENUM. *Symbol*, Mo. *Atomic Weight*, 92.—A metal occurring in small quantity as a sulphide (*molybdenite*), and as molybdate of lead (*wulfenite*). The native sulphide was first distinguished from plumbago, which it much resembles, by Scheele in 1778; the metal was first prepared from the trioxide by Hjelm in 1782.

The most complete investigations of the properties and combinations of this metal have been made by Berzelius (Pogg. Ann. iv. 153; vi. 361, 369; vii. 261); Svanberg and Struve (J. pr. Chem. xliv. 257; Jahresb. 1847–48, p. 408); Struve

(J. pr. Chem. lxi. 449; Jahresb. 1854, p. 346); **Blomstrand** (J. pr. Chem. lxxi. 449; lxxvii. 88; lxxxii. 433; Jahresb. 1857, p. 191; 1859, p. 164; 1861, p. 239); and **H. Schultze** (Ann. Ch. Pharm. cxxvi. 49; Jahresb. 1863, p. 217). The name molybdenum is derived from *μολύβδαινα* or *molybdæna*, applied by Dioscorides and Pliny to galena and other lead-compounds.*

Preparation.—Metallic molybdenum is prepared:—1. By exposing either of the oxides, or molybdate of ammonium, or acid molybdate of potassium, to a full white heat in a crucible lined with charcoal. The reduction is easily effected, and may even be performed on charcoal before the blowpipe with carbonate of sodium; but to obtain a fused button of the metal, a very strong heat is required (**Berzelius**).—2. By passing dry hydrogen gas over either of the oxides of molybdenum heated to whiteness in a porcelain tube. (**Berzelius.**)

Properties.—Molybdenum reduced by hydrogen is a grey pulverulent mass which acquires a metallic lustre by trituration, and conducts electricity. By fusion in a Deville's blast-furnace, it is obtained as a white mass, with nearly silvery lustre, harder than topaz, and of specific gravity 8·6. (**Debray**, Compt. rend. xlvi. 1098.)

Molybdenum is unalterable in the air at ordinary temperatures, but when slowly heated it acquires, first a brownish-yellow, then a blue tarnish, and finally takes fire (? the pulverulent metal) and burns to molybdic trioxide (**Berzelius**). It is rapidly oxidised by fusion with *nitre*, slowly by *hydrate of potassium*, and it is not dissolved by boiling potash-lye. It dissolves in *nitric acid* with evolution of nitrous fumes, and in hot strong *sulphuric acid* with evolution of sulphurous anhydride. If the acids are used in small quantity only, the metal is converted into molybdic oxide; with a larger proportion of sulphuric acid, the blue oxide is formed; and with a larger proportion of nitric acid the product is molybdic acid, which is also partially deposited in the solid state. Molybdenum is likewise oxidised and dissolved by *chlorine-water* and by a mixture of *nitric* with *sulphuric* or *hydrochloric acid*. It is dissolved by boiling aqueous *arsenic acid*, slightly also by *phosphoric* and *boric acids*; not by hydrochloric or dilute sulphuric acid. It reduces the oxides of *silver* and *mercury* when triturated with them. Ignited in a stream of *aqueous vapour*, it is oxidised, with separation of hydrogen.

Combinations.—Molybdenum enters into combination as a diatomic, tetratomic, hexatomic, and sometimes also as a tri-atomic radicle: thus it forms the oxides $Mo''O$, $Mo^{iv}O^2$, $Mo^{vi}O^3$, the chlorides, $Mo''Cl^2$ and $Mo^{iv}Cl^4$; the bromides, $Mo''Br^2$, $Mo'''Br^3$, the bromo-chloride, $Mo^{vi}Br^4Cl^2$, the oxychloride, $Mo^{iv}Cl^2O$, &c. Its exact position in the metallic series is not yet exactly ascertained, inasmuch as its specific heat has not been determined, and those of its compounds which are volatile, assume the gaseous state at too high a temperature to allow of the determination of their vapour-densities (see page 968).

MOLYBDENUM, ALLOYS OF. Molybdenum unites with tin, lead, iron, copper, silver, gold, and platinum, rendering them less fusible, more brittle, and, except in the case of silver, whiter. *Molybdide of copper* is of a pale, copper-red colour, malleable if the molybdenum is not in excess. With 2 pts. of *gold*, molybdenum forms a black, brittle globule.—*Molybdide of iron* constitutes the so-called "bears" found on the hearths of copper-furnaces (p. 368). Equal parts of molybdenum and *platinum* yield a hard, brittle, shapeless lump, having a light grey colour and metallic lustre, and appearing compact on the fractured surface. 4 pts. platinum with 1 pt. molybdenum form a hard, brittle, bluish-grey alloy, having a granular fracture (**Hjelm**).—The alloy of 1 pt. *silver* and 2 pts. molybdenum is grey, granular, and brittle.

Molybdide of Aluminium, $Al^{12}Mo$, is obtained by dissolving molybdic acid in hydrofluoric acid, evaporating to dryness, and fusing the residue with a mixture of 30 pts. cryolite, 30 pts. of a mixture of the chlorides of sodium and potassium in equivalent proportions, and 15 pts. aluminium, at a strong red heat. On treating the resulting regulus with soda-lye, there remains a crystalline powder coloured black by a film of metallic molybdenum, but assuming an iron-grey colour when treated with nitric acid, and appearing under the microscope to consist of rhombic prisms. It acquires a steel-blue tarnish when ignited in the air, and dissolves easily in hot nitric and hydrochloric acids. (**Wöhler**, Ann. Ch. Pharm. cxv. 102.)

MOLYBDENUM, BROMIDES OF. (**Blomstrand**, J. pr. Chem. lxxvii. 88; lxxxii. 433; Jahresb. 1859, p. 164; 1861, p. 239.) When bromine-vapour is passed over strongly heated molybdenum, an oxybromide is first formed, then a greyish-green sublimate of tribromide close to the heated part of the tube, the metal at the same time acquiring a yellowish-red colour and being at last completely converted into dibromide; between these two products there are also found isolated shining needles of the tetrabromide, of a pure black colour.

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* "Est et molybdæna, quam alio loco galenam vocavimus, vena argenti plumbique communis." (Pliny.)

The *Dibromide* or *Molybdous bromide*, $Mo''Br^2$, is produced, as just stated, by direct combination of its elements, also by heating the tribromide. It is a non-volatile, amorphous, reddish-yellow body, which is not perceptibly attacked by hydrochloric, nitric, or even boiling nitromuriatic acid, but dissolves easily and completely when heated with dilute caustic alkalis, forming a yellow solution containing molybdous oxybromide:

$$3MoBr^2 + 2KHO = 2KBr + H^2O + Mo^3Br^4O.$$

Concentrated solutions of caustic alkalis decompose the bromide completely, with precipitation of a black hydrated oxide.

The yellow solution above mentioned, when exposed to the air, gradually deposits small shining golden yellow crystals of a hydrated molybdous oxybromide, $\overset{''}{Mo}{}^3Br^4O.9H^2O$; but when neutralised with an oxygen-acid, it yields a dark yellow, flocculent or granular precipitate of the same oxybromide with a smaller quantity of water, $\overset{''}{Mo}{}^3Br^4O.3H^2O$. The oxybromide dissolves with yellow colour in alkalis and in the stronger oxygen-acids, and from the acid solutions thus obtained, the bromine is not precipitated by silver salts.—The solution of the oxybromide in dilute aqueous alkalis forms with *hydrobromic*, *hydrochloric*, or *hydriodic acid*, a yellow precipitate, insoluble in acids, but soluble in alkalis, and consisting of $\overset{''}{Mo}{}^3Br^6.3H^2O$, $\overset{''}{Mo}{}^3Br^4Cl^2.3H^2O$ or $\overset{''}{Mo}{}^3Br^4I^2.3H^2O$.—Blomstrand regards all these compounds as containing the diatomic radicle, *bromomolybdenum*, $MoBr^4$, *e.g.*, the oxybromide, $(MoBr^4)''O$, the chlorobromide, $(MoBr^4)''Cl^2$, &c. (See page 1030.)

The *Tribromide*, $Mo'''Br^3$, or *Molybdoso-molybdic bromide*, $MoBr^2.MoBr^4$, is produced as above mentioned, by direct combination, or with greater facility by passing bromine-vapour over a heated mixture of molybdic oxide and charcoal. It is sometimes obtained in separate crystals, but more frequently in blackish-green masses consisting of delicate, capillary, interlaced needles. It is difficult to sublime, and at a bright red heat is resolved into the dibromide and free bromine. It is not even wetted by water, and not attacked by boiling hydrochloric acid or by cold dilute nitric acid. Dilute alkalis act upon it slowly, and at the boiling heat decompose it completely, with separation of black molybdic hydrate.

The *Tetrabromide* or *Molybdic bromide*, $Mo^{iv}Br^4$, formed also by direct combination (p. 1028), is fusible and volatile, forming a brown-red vapour; it deliquesces in the air to a black liquid; and forms with water a yellow-brown solution, from which alkalis throw down molybdic hydrate of a rusty yellow colour. It is easily resolved by heat into the dibromide and free bromine, the temperatures at which it is formed and decomposed being very close together.

The *hexbromide*, $Mo^{vi}Br^6$, has not been obtained, but the corresponding *oxybromide*, $Mo^{vi}Br^2O^2$, is produced by passing bromine-vapour over heated molybdic oxide, MoO^2, or by heating molybdic trioxide with boric, or phosphoric anhydride, and fusing the pulverised mass with bromide of potassium, *e.g.*:

$$MoO^3 + B^2O^3 + 2KBr = 2KBO^2 + MoBr^2O^2.$$

When quickly sublimed, it forms indistinct crystalline scales; but by slow sublimation it may be obtained in more distinctly developed crystalline plates of yellow-red colour and fatty lustre, which deliquesce in contact with the air, and form a colourless solution in water.

MOLYBDENUM, CHLORIDES OF. Molybdenum forms three chlorides, analogous to the bromides. The tri-chloride and tetrachloride were first prepared by Berzelius, who also obtained the dichloride in solution; these compounds have been more fully examined by Blomstrand, who has also obtained the anhydrous dichloride and several oxychlorides.

Dichloride or *Molybdous Chloride*, $Mo''Cl^2$.—This compound is formed, together with the other chlorides, by passing chlorine-gas over heated molybdenum. It may be prepared, though not in a state of purity, by exposing the trichloride to a moderate heat in an atmosphere of carbonic anhydride, or other gas which does not act upon it, or by heating metallic molybdenum with calomel; also, though in very small quantity, by passing chlorine-gas largely diluted with carbonic anhydride over moderately heated molybdenum; it is likewise formed in small quantity, together with the tetrachloride, by passing chlorine over a heated mixture of molybdic oxide and charcoal when the temperature is very high. (Blomstrand.)

Molybdous chloride is obtained, in solution, by saturating hydrochloric acid with molybdous hydrate. The dark-brown solution yields on evaporation a black mass which redissolves almost entirely in water, but on evaporation in vacuo, gives off hydrochloric acid and water, and is converted into a black pulverulent oxychloride. (Berzelius.)

The anhydrous dichloride is an amorphous powder of dull yellow colour, inclining to greenish from the presence of impurities. It behaves with *alkalis* like the dibromide, but dissolves easily and completely in *hydrochloric*, *hydrobromic*, and *hydriodic acids*. The alkaline solution when exposed to the air, deposits **molybdous oxychloride**, $\overset{\prime\prime}{\mathrm{Mo}}{}^2\mathrm{Cl^4O}$, in combination with water, sometimes in very small crystals, but generally as an amorphous gummy precipitate. *Acids* (especially acetic acid) added to the same solution, throw down the hydrated oxychloride, $\overset{\prime\prime}{\mathrm{Mo}}{}^2\mathrm{Cl^4O.3H^2O}$, in the form of light yellow flocks, which when recently precipitated, and washed with water, dissolves easily in the stronger acids. (Blomstrand.)

The hydrated oxychloride boiled with hydrobromic, hydriodic and hydrochloric acids, yields solutions which deposit compounds of exactly analogous constitution, having the oxygen replaced by an equivalent quantity of bromine, iodine or chlorine. With *hydrobromic acid*, the chlorobromide, $\mathrm{Mo^2Cl^4Br^2.3H^2O}$, is obtained, in thin reddish-yellow scales, insoluble in water, but soluble in alcohol; the alcoholic solution highly concentrated at 100°, deposits short prismatic crystals containing $\overset{\prime\prime}{\mathrm{Mo}}{}^2\mathrm{Cl^4Br^2.6H^2O}$, easily soluble in water and forming a solution which, after a while, becomes turbid unless it contains a large quantity of free acid), and deposits a granular powder. Similarly with *hydriodic acid*, the compound $\overset{\prime\prime}{\mathrm{Mo}}{}^2\mathrm{Cl^4I^2.3H^2O}$ is obtained, as a scaly crystalline substance, insoluble in water; also $\overset{\prime\prime}{\mathrm{Mo}}{}^2\mathrm{Cl^4I^2.6H^2O}$, which resembles the corresponding bromine-compound, but forms darker-coloured crystals. The corresponding *chlorine-compounds*, $\overset{\prime\prime}{\mathrm{Mo}}{}^2\mathrm{Cl^6.3H^2O}$ and $\overset{\prime\prime}{\mathrm{Mo}}{}^2\mathrm{Cl^6.6H^2O}$ (or $\overset{\prime\prime}{\mathrm{Mo}}\mathrm{Cl^2.H^2O}$ and $\overset{\prime\prime}{\mathrm{Mo}}\mathrm{Cl^2.2H^2O}$), are obtained in like manner, the former in thin scales insoluble in water, the latter in light yellow slender needles or prisms, which also dissolve in water, forming a solution which soon becomes turbid. The acid solutions of these compounds may be repeatedly evaporated to dryness, even in contact with the air without perceptible decomposition. The solid compounds heated in an atmosphere of carbonic anhydride, first give off nothing but water; but afterwards, if the heat be quickly raised, a certain quantity of acid is given off, so that the residue always contains more or less of the corresponding oxychloride, or even molybdous oxide, *e.g.*

$$\mathrm{Mo^2Cl^4Br^2} + \mathrm{H^2O} = \mathrm{Mo^2Cl^4O} + 2\mathrm{HBr}$$

$$\text{and } \mathrm{Mo^2Cl^4Br^2} + 3\mathrm{H^2O} = 3\mathrm{MoO} + 2\mathrm{HBr} + 4\mathrm{HCl}.$$

The same decompositions take place, but to a greater extent, when these compounds are heated in contact with moist air.

The haloïd molybdous compounds just described unite with the haloïd salts of potassium and ammonium, forming double salts having the composition $\mathrm{Mo^2Cl^6.KCl}$; $\mathrm{Mo^2Cl^4Br^2.2NH^4Br}$, $\mathrm{Mo^2Cl^4Br^2.2KBr}$, &c., which crystallise out almost completely from their acid solutions on cooling. These double salts vary in colour from shining straw-yellow (the chlorine-salts), to deep yellowish-red (the iodine-salts); they are of various, usually prismatic form; are decomposed by pure *water*, the alkali-metal salt dissolving, while the molybdous compound ($\mathrm{Mo^2Cl^4Br^2}$, for example) separates in combination with $3\mathrm{H^2O}$; but dissolve without decomposition in water containing free acid. *Alcohol* dissolves some of them ($\mathrm{Mo^2Cl^4Br^2.2NH^4Br}$, for example) without decomposition, whereas from others (as $\mathrm{Mo^2Cl^4Br^2.2KBr}$) it dissolves the molybdous compound, and leaves the salt of the alkali-metal. *Nitrate of silver* added to the solutions of these double salts, throws down only half the amount of halogen contained in them (*e.g.* from $\mathrm{Mo'Cl^4Br^2.2KBr}$, only the 4 at. bromine, and from $\mathrm{Mo^2Cl^6.2KCl}$, or $\mathrm{Mo^2Cl^4Cl^2.2KCl}$, only 4 at. chlorine); moreover their acid solutions are not decomposed by sulphydric acid, even after a day's contact (in the alkaline solutions it produces a slow decomposition), and they are not precipitated by ferro-cyanide of potassium. From these reactions, and from the composition of the double salts, Blomstrand infers that all these compounds contain the diatomic radicle, *chloromolybdenum* $\mathrm{Mo^2Cl^4}$, that molybdous chloride is $(\mathrm{Mo^2Cl^4})''\mathrm{Cl^2}$, the oxychloride $(\mathrm{Mo^2Cl^4})''\mathrm{O}$, the chlorobromide $(\mathrm{Mo^2Cl^4})\mathrm{Br^2}$, &c.

Trichloride, $\mathrm{Mo'''Cl^3}$, or ***Molybdoso-molybdic chloride***, $\mathrm{MoCl^2.MoCl^4}$. This compound is obtained, though not in the pure state, by passing the vapour of molybdic chloride, $\mathrm{MoCl^4}$, over heated molybdenum. Berzelius, who prepared it in this manner, but does not appear to have analysed it, regarded it as the dichloride; but according to Blomstrand's analysis, the compound thus obtained has nearly the composition $\mathrm{MoCl^3}$. The trichloride is more easily obtained by passing hydrogen gas over the tetrachloride heated in a glass tube by a spirit-lamp; or better, by passing the vapour of the tetrachloride mixed with carbonic anhydride, through a tube, one part of which is very strongly heated; the trichloride then collects behind this portion, as a thick homogeneous crust (Blomstrand). It has a dark copper-red colour, and when heated to the melting point of glass, in a vessel which does not allow access of air, it volatilises and forms a confusedly crystalline, dark brick-red sublimate (Berzelius). It is insoluble in *water*, but colours that liquid reddish when suspended in it; insoluble also in dilute *hydrochloric acid*. When digested with *potash* it yields chloride of potassium and an insoluble blackish-brown hydrated oxide of molybdenum. (Berzelius.)

Tetrachloride or *Molybdic chloride*, $\text{Mo}^{\text{iv}}\text{Cl}^4$. This compound, discovered by Berzelius, is produced when chlorine gas, free from air, is passed over gently heated molybdenum. The metal then takes fire and burns on the surface for a few seconds; but this effect soon ceases and a dark red gas is formed, which condenses on the cold parts of the vessel in dark coloured metallic-shining crystals having very much the aspect of iodine. Blomstrand prepares it by the action of chlorine on strongly heated molybdic sulphide (the native sulphide). The crystals are very fusible (Berzelius), somewhat difficult of fusion (Blomstrand), and sublime at a moderate heat. When exposed to the air, they fume at the first instant, and then deliquesce, the original black colour of the liquid passing through blue-green, greenish-yellow, and dark red into yellow. When kept in a vessel containing air, they absorb oxygen and yield a sublimate consisting of an oxychloride.

Molybdic chloride when thrown into water, dissolves with such violence that the liquid effervesces and boils, as if a gas were given off, which however is not the case. A small quantity of the chloride drenched with a large quantity of water forms a solution which soon turns green or blue from the oxidising action of the air; a stronger solution is more permanent, and may be evaporated to dryness at a gentle heat without decomposition, the tetrachloride then remaining as a black mass. Molybdic chloride may also be obtained in solution by digesting the metal in hydrochloric acid, and adding nitric acid from time to time till the liquid acquires a red-brown colour, or by digesting molybdic anhydride and pulverised molybdenum (or metallic copper) in hydrochloric acid, till all the molybdic anhydride is dissolved and the liquid has become red. In all these solutions, ammonia forms a precipitate of molybdic hydrate.

Ammonio-molybdic chloride is obtained, according to Berzelius, by mixing a solution of molybdic chloride with ammonia, till the precipitate just begins to be permanent, and leaving the solution to evaporate, the double salt then separating in small brown crystals which decompose in contact with air.

A solution of molybdic chloride saturated with sal-ammoniac and left to evaporate over oil of vitriol, first deposits brown crystals of sal-ammoniac; and the mother-liquor ultimately yields green octahedrons of the double salt $3\text{MoCl}^4.2\text{NH}^4\text{Cl}.6\text{H}^2\text{O}$, which soon deliquesce in moist air to a black liquid becoming reddish-yellow when diluted, and yielding with ammonia a yellowish-red precipitate of molybdic hydrate. (Blomstrand.)

MOLYBDENUM, CHLOROBROMIDES OF. This compound, $\overset{\prime\prime}{\text{Mo}}{}^3\text{Br}^4\text{Cl}^2$, is obtained by the action of hydrochloric acid on molybdous oxybromide, and $\overset{\prime\prime}{\text{Mo}}{}^3\text{Cl}^4\text{Br}^2$ by that of hydrobromic acid on molybdous oxychloride. (Blomstrand, pp. 1029, 1030.)

MOLYBDENUM, DETECTION AND ESTIMATION OF. 1. *Blowpipe reactions.*—Molybdic trioxide heated on charcoal in the outer flame is volatilised and forms a white crystalline sublimate on the charcoal; in the inner flame it may be reduced (even without carbonate of sodium) to metallic molybdenum, which is separated as a grey powder on levigating the charcoal. With *borax*, all the oxides of molybdenum give, in the outer flame, a bead which is yellow while hot, and colourless on cooling; in the inner flame, a dark brown bead, which is opaque if excess of molybdenum is present. By long continued heating, the molybdic oxide may be separated in dark brown flakes, floating in the clear yellow glass. With *microcosmic salt* in the outer flame, all oxides of molybdenum give a bead which is greenish while hot, and colourless on cooling; in the inner flame, a clear green bead from which molybdic oxide cannot be separated by continued heat.

2. *Reactions in Solution.*—*a.* Solutions of molybdous salts obtained by dissolving molybdous oxide in acids are opaque and almost black. They yield with *sulphydric acid* a brown-black precipitate, and with *sulphide of ammonium* a yellowish-brown precipitate of sulphide of molybdenum easily soluble in sulphide of ammonium. *Alkalis* and *alkaline carbonates* produce a brownish-black precipitate of molybdous hydrate insoluble in caustic alkalis, slightly soluble in the neutral carbonates, easily soluble in acid carbonate of potassium or carbonate of ammonium. *Ferrocyanide* and *ferricyanide of potassium* form dark brown precipitates insoluble in excess. *Phosphate of sodium* forms a white precipitate.

β. Solutions of molybdic salts have a reddish-brown colour. When heated in the air, they have a tendency to become blue by oxidation. In contact with metallic *zinc*, they first blacken and then yield a black precipitate of molybdous hydrate. Their reactions with *alkalis*, *sulphydric acid*, &c., are similar to those of the molybdous salts, excepting that the precipitates are lighter in colour.

γ. Molybdates are colourless unless they contain a coloured base. Solutions of the alkaline molybdates yield with *acids* a precipitate of molybdic acid, soluble in excess of the precipitant. They are coloured yellow by *sulphydric acid*, from formation of a sulphomolybdate of the alkali-metal R^2MoS^4, and then yield with acids a brown precipitate of trisulphide of molybdenum. This is an extremely delicate test for molybdic acid. They form white precipitates with the salts of the *earth-metals*, and precipitates of various colours with salts of the *heavy metals ; e.g.* white with lead and silver salts ; yellow with ferric salts ; and yellowish-white with mercurous salts.—*Stannous chloride* produces immediately a greenish-blue precipitate, soluble in hydrochloric acid, forming a green solution, which turns blue on the addition of a very small quantity of the tin-solution. *Mercurous nitrate* forms a yellowish-white precipitate, soluble in nitric acid, blackened by ammonia. When *tribasic phosphoric acid*, or a liquid containing it, is added to the solution of molybdate of ammonium, together with an excess of hydrochloric acid, the liquid turns yellow, and after a while deposits a yellow precipitate of molybdic acid combined with small quantities of phosphoric acid and ammmonia. This precipitate is soluble in ammonia and likewise in excess of the phosphate. The reaction is therefore especially adapted for the detection of small quantities of phosphoric acid. The dibasic and monobasic phosphates do not produce the yellow precipitate. *Arsenic acid* gives a similar reaction.

3. *Quantitative Estimation, and Separation.* When molybdenum occurs in the form of trioxide or molybdic anhydride (MoO^3), the best mode of estimating it is to convert it into the di-oxide, MoO^2, by ignition in an atmosphere of hydrogen. This oxide, which is not at all volatile, may then be weighed. When molybdic acid exists in solution in ammonia or in other acids, the solution must be carefully evaporated by dryness and the residue treated as above.

Molybdenum is separated from most metals by its solubility in *sulphide of ammonium*. The filtered solution containing sulphomolybdate of ammonium is then treated with an excess of very dilute nitric acid, to precipitate the trisulphide; the precipitate is collected on a weighed filter and its weight determined, after which a known quantity of it is ignited in an atmosphere of hydrogen, to convert it into the disulphide, MoS, from the weight of which the amount of molybdenum is calculated.

From arsenic, molybdenum may be separated by converting the arsenic into arsenic acid, and precipitating it by a magnesium-salt (i. 367). Antimony may be separated from molybdenum by the same process which serves to separate it from arsenic and tin (i. 369), the alkaline molybdates, like the arsenates and stannates, being soluble in water. For the separation of molybdenum from tungsten, see TUNGSTEN.

Molybdic acid is separated from the earths, by fusing the compound with *carbonate of sodium*, and digesting the fused mass in water, which dissolves molybdate of sodium and leaves the earth as carbonate.

From the fixed alkalis, molybdic acid may be separated by precipitation with *mercurous nitrate*. The precipitate is thoroughly washed with a dilute solution of the mercurous nitrate, then dried and ignited at a moderate heat in a stream of hydrogen, whereby it is reduced to molybdic oxide.

4. *Atomic Weight of Molybdenum.* Berzelius, in 1818 (Schw. J. xxii. 51), endeavoured to determine the atomic weight of this metal by the quantity of molybdate of lead, $PpbMO^4$, obtained by precipitation from a known weight of the nitrate; in this way he obtained for molybdenum the number 96, which however he regarded as only an approximation.

Svanberg and Struve (Ann. Ch. Pharm. lxviii. 209), from an extensive series of experiments, considered that the most accurate results were obtained by roasting the disulphide, MoS^2, in air. They found in ten experiments, that the artificially prepared disulphide lost by roasting, from 9·929 to 10·356 per cent. of its weight; whence, taking the atomic weight of sulphur at 32, they obtained, as a mean result, the number 92·14 ; but the results of the individual experiments (even excluding the three which differed most widely from the rest) varied from 80·88 to 97·15, so that no great dependence can be placed on the mean result.

Berlin, in 1850 (Ann. Ch. Pharm. lxxvi. 272), analysed the ammonium-salt,

$$(NH^4)^2Mo^5O^{17}.3H^2O \text{ or } 2NH^4O.5MoO^3.3H^2O,$$

and found the quantity of molybdic anhydride, MoO^3, left on igniting it, to vary in four experiments, only between 81·555 and 81·612: mean 81,581, whence he obtains for molybdenum the number 92, nearly the same as that found by Svanberg and Struve.

On the other hand, Dumas (Ann. Ch. Phys. [3] lx. 129), by reducing crystallised molybdic anhydride in a current of hydrogen, obtained in six experiments, values of Mo between 95·2 and 96·2: mean 95·7; he regards 96 as the true atomic weight of molybdenum, which is the same as that originally found by Berzelius.

MOLYBDENUM, FLUORIDES OF. *a. Molybdous Fluoride.*—Molybdous oxide dissolves in hydrofluoric acid, forming a purple-red liquid which dries up at a gentle heat to a varnish of the same colour; this residue when more strongly heated becomes darker in colour, and partly insoluble in water.

Potassio-molybdous fluoride is precipitated in pale red flocks on mixing a solution of molybdous fluoride with fluoride of potassium. It is dissolved by water containing a little free acid, and separates, during evaporation or on cooling, as a dark rose-coloured powder, which becomes lighter when dry. The *ammonium-salt* is exactly similar; the *sodium-salt* is more soluble.

β. Molybdic Fluoride.—The solution of molybdic hydrate in aqueous hydrofluoric acid is red, unless the acid is in very large excess, in which case it is almost colourless. After gentle evaporation, whereby it is soon rendered blue if the acid is not in excess, it leaves a black crystalline residue (of molybdic fluoride?), which redissolves perfectly in water, forming a red solution; but if somewhat more strongly heated, loses acid, and when dissolved in water, leaves a residue of molybdic oxide. (Berzelius.)

Double salts of molybdic fluoride are obtained by mixing the solution just described with the fluorides of the alkali-metals. They are rusty yellow powders, somewhat soluble in water.

The blue oxide of molybdenum yields with hydrofluoric acid a deep blue solution which does not crystallise. (Berzelius.)

γ. Hexfluoride. Molybdic trioxide dissolves readily and abundantly in aqueous hydrofluoric acid. The colourless solution has a sour and disagreeable metallic taste, and yields, on evaporation, a yellowish syrup which exhibits no signs of crystallisation; assumes a greenish or bluish tint when heated, in consequence of minute organic particles falling into it; redissolves but imperfectly in water after evaporation to complete dryness; and leaves an insoluble compound of molybdic trioxide with a small proportion of hydrofluoric acid, or of molybdic trioxide with hexfluoride of molybdenum, which, though soluble to a certain extent in pure water, is precipitated from it by the first-mentioned acid solution.

Several combinations exist of hexfluoride of molybdenum with the more basic metallic fluorides; they are not, however, known in the free state, but only in combination with salts of molybdic acid: *e. g.*, $K^2MoO^4.K^2MoF^6$. (Berzelius.)

MOLYBDENUM GLANCE. Native sulphide of molybdenum (p. 1043).

MOLYBDENUM, IODIDES OF. Molybdenum and iodine do not act on one another, even at a red heat. By dissolving molybdous hydrate in hydriodic acid, a solution of *molybdous iodide* is obtained resembling that of molybdous chloride (p. 1029).

Molybdic iodide is obtained in solution by saturating hydriodic acid with molybdic hydrate. The solution is red, and yields by evaporation in contact with the air, a crystallised salt, which is red by transmitted, brown by reflected light. It decomposes at a high temperature, giving off hydriodic acid and leaving molybdic oxide. The residue left on spontaneous evaporation redissolves in water. (Berzelius.)

MOLYBDENUM, IODOBROMIDE and **IODOCHLORIDE OF.** $Mo^3Br^4I^2$ and $Mo^3Cl^4I^2$.—These compounds are obtained by the action of hydriodic acid on molybdous oxybromide and oxychloride respectively (pp. 1029, 1030).

MOLYBDENUM, NITRIDES and **AMIDES OF.** (Tuttle, Ann. Ch. Pharm. ci. 285. Uhrlaub, Pogg. Ann. ci. 605; Jahresb. 1857, p. 194.)—These compounds, which have not been very exactly investigated, are obtained by passing ammonia-gas over molybdic trioxide, or the chlorides of molybdenum, at high temperatures. Tuttle, by heating molybdic chloride in ammonia-gas till the resulting chloride of ammonium was volatilised, obtained a black sintered mass containing 82·8 per cent. molybdenum, probably consisting of $2MoN.MoH^4N^2$.

Uhrlaub has also obtained compounds of similar constitution by the action of dry ammonia-gas on molybdic chloride. The action takes place even at ordinary temperatures, and is attended with sufficient evolution of heat to partially fuse the mass and drive off chloride of ammonium. On subsequently applying a gentle heat, the product becomes viscid, and soon solidifies to a black tumefied mass, exhibiting stellate groups of brownish crystals on the colder parts; when completely freed from sal-ammoniac by rapid washing with water, and then dried in a vacuum over oil of vitriol, it exhibited a composition expressible by the formula $Mo^5H^4N^{10}$ or $4MoN^2. MoN^2H^4$. This compound burns brightly in oxygen gas, with formation of water, and gives off ammonia when ignited in hydrogen gas, or fused with hydrate of potassium. A compound resembling the preceding in external appearance, but consisting of $8MoN.MoH^4N^2$, was obtained by heating molybdic chloride in ammonia-gas, the heat being at last raised to low redness. Molybdic chloride gradually heated to redness in a stream of ammonia-gas, yielded, but not always, the compound Mo^3N^2, which resembled the two preceding in most respects, but had a greyer colour; sometimes, however, nitrides were obtained, intermediate in composition between Mo^3N^2 and Mo^2N^2. All these compounds, when heated to whiteness in ammonia-gas, yield metallic molybdenum.

Molybdous chloride treated with ammonia-gas yields the same compounds, together with another, which, according to Uhrlaub, is analogous in composition to some of the platinum-bases.

Nitrides and amides of molybdenum are likewise obtained by the action of ammonia-gas on molybdic anhydride. The reaction appears to be very complicated, the products MoN^2, MoH^4N^2, Mo^2N^2, and Mo^3N^3, being obtained in different proportions according to the temperature, and often uniting together to form compounds varying greatly in composition.

MOLYBDENUM, OXIDES OF. Molybdenum forms three oxides, having the following composition:

Protoxide or Molybdous oxide	MoO
Dioxide or Molybdic oxide	MoO^2
Trioxide or Molybdic anhydride	MoO^3

The first two are basylous and form salts with acids; the third also unites loosely with some of the stronger acids, but it is decidedly of a chlorous character, uniting readily with the more basylous metallic oxides, and forming definite crystallisable salts called Molybdates. There is also an oxide (or perhaps more than one) intermediate between the di- and tri-oxide, which may be regarded as a molybdic molybdate.

Protoxide or **Molybdous oxide,** MoO. This oxide is produced by bringing the di- or tri-oxide, in presence of one of the stronger acids, in contact with any of the metals which are capable of decomposing water. Thus, when zinc is immersed in a concentrated solution of an alkaline molybdate mixed with a quantity of hydrochloric acid sufficient to redissolve the molybdic acid which is at first thrown down, the liquid becomes first blue, then reddish-brown, and finally black, and contains chloride of zinc and molybdous chloride. To separate the molybdenum from the zinc, ammonia is then added to the liquid in quantity just sufficient to precipitate the molybdenum, as black molybdous hydrate, while the zinc remains in solution. The precipitate, however, carries down with it a certain quantity of zinc-oxide, from which it may be freed by washing with ammonia; but it is difficult in this way to obtain molybdous hydrate quite free from zinc. A better mode of preparation is to agitate the acidulated solution of the molybdate with an amalgam of potassium containing only a very small quantity of potassium, and precipitate the resulting solution of molybdous chloride with ammonia as before.

Anhydrous molybdous oxide may be obtained by drying the hydrate over oil of vitriol in a vacuum, and then igniting it out of contact with the air; or directly by digesting the fused or sublimed trioxide for a considerable time with hydrochloric acid and zinc.

Anhydrous molybdous oxide is perfectly black by ordinary daylight; but that prepared by the last method exhibits a dark brass-yellow colour, when exposed to the direct rays of the sun; it also exhibits the crystalline form of the trioxide from which it has been prepared, and oxidises in the air more rapidly than that which is obtained by igniting the hydrate. The anhydrous oxide, when heated nearly to redness, emits a vivid but momentary light, indicating its passage into another modification. It is insoluble in acids, but the hydrate dissolves slowly, forming the molybdous salts, the solutions of which are black or purple, and nearly opaque, except when largely diluted, in which case they are transparent, and have a greenish-brown colour; their taste is astringent but not metallic; when exposed to the air, they oxidise, but not so rapidly as the molybdic salts.

Dioxide or Molybdic Oxide. MoO^2.—This oxide is obtained: 1. By igniting molybdic hydrate in a vacuum (Berzelius).—2. By exposing the trioxide in a stream of hydrogen to a heat not greater than that of an ordinary spirit-lamp (Svanberg). It is also said to be produced by igniting molybdate of ammonium in a close vessel, or by igniting a mixture of potassic or sodic molybdate with sal-ammoniac, and dissolving out the soluble chloride with water; but the oxide thus obtained appears to be contaminated with nitrate of molybdenum.

Molybdic oxide is red-brown. It is not attacked by aqueous hydrofluoric or hydrochloric acid, or by hydrochloric acid gas at a red heat. Sulphuric acid or solution of acid tartrate of potassium takes up only traces of it, even on continued digestion, and the residue left after decanting the liquid is not attacked by fresh quantities of sulphuric acid or solution of cream of tartar. Molybdic oxide is further oxidised by ignition in the air, or by treatment with nitric acid. Caustic potash-solution neither oxidises nor dissolves it.

Molybdic hydrate is obtained by precipitating a solution of molybdic chloride or other molybdic salt with ammonia, which must be added in excess, as otherwise a soluble basic salt will be formed, especially with the chloride. The hydrate itself is also somewhat soluble in pure water, so that, in very dilute solutions, ammonia does not form any precipitate until sal-ammoniac is added. For the same reason, the washing must not be carried too far, and is best finished with water containing alcohol. The washed hydrate may be pressed between paper and dried in a vacuum. It has a rusty brown colour, just like that of ferric hydrate precipitated by ammonia. When exposed in the moist state to the air on filtering paper, it acquires a darker colour and shining surface, and begins to deliquesce, passing into a higher and much more soluble oxide. It dissolves, as already observed, in a large quantity of water, forming a dark red solution, which gelatinises when kept for three or four weeks in a closed vessel, reddens litmus, a property likewise retained by the hydrate precipitated from it by sal-ammoniac, and has a somewhat astringent taste, with metallic after-taste. This solution, when left to evaporate spontaneously, first gelatinises and then dries up to a dark brown, nearly black mass, green and blue on the edges, which is no longer soluble in water. The hydrate is insoluble in caustic potash, but dissolves in aqueous neutral carbonate of potassium, and more easily in the acid carbonate, from which solution it is partially precipitated on boiling. It dissolves also in carbonate of ammonium, and is completely precipitated therefrom by boiling; the precipitate is denser and of a lighter yellow colour than that obtained with caustic ammonia, but dissolves, like the latter, when washed with water. A solution of molybdic oxide in an alkaline carbonate is converted by atmospheric oxidation into a molybdate of the alkali-metal.

Molybdic hydrate dissolves in *acids*, forming the molybdic salts. These salts may also be obtained by digesting an excess of metallic molybdenum with the acid in which it is to be dissolved, and adding nitric acid drop by drop till the other acid is saturated with molybdic oxide; or by digesting an excess of molybdenum with molybdic anhydride, and the acid which is required to dissolve the resulting molybdic oxide—hydrochloric acid, for example—till the blue colour first produced changes to reddish-brown; or lastly, by digesting molybdic anhydride with copper and an acid, which in that case dissolves cupric and molybdic oxides together. The molybdic salts, in the anhydrous state, are almost black, but when hydrated they are red, and yield reddish-brown solutions in water. They have a rough, somewhat astringent and subsequently metallic taste. Their solutions when heated in contact with the air, have a tendency to become blue by oxidation. [For their behaviour with reagents, see p. 1039.]

The oxides intermediate between the di- and tri-oxides will be described as molybdic molybdates (p. 1039).

Trioxide. *Molybdic Anhydride, Anhydrous Molybdic acid,* MoO^3.—This oxide occurs native, as molybdic ochre or molybdin, forming an earthy coating on the native sulphide, sometimes also independently; at Altenberg in Saxony it occurs in rhombic prisms of 136° 48′ (Breithaupt, Jahresb. 1858, p. 683). It may be formed artificially by exposing molybdenum or its lower oxides, or molybdic sulphide, to long-continued heat in contact with the air, by fusing the same substances with nitre, or by heating the metal or its oxides in an atmosphere of aqueous vapour, or with hydrate of potassium.

Preparation. α. From *Molybdic Sulphide.*—The precipitated sulphide, or the native mineral finely pulverised, is roasted, with continued stirring, in an open crucible placed in a slanting position, so that the air may easily play upon its surface. The native sulphide, however, generally contains alumina, oxide of copper, and phosphoric acid, the separation of which from the product is very troublesome. Hence it is better to heat the mineral in lumps in an open glass tube, through which a stream of air is drawn by an aspirator; the trioxide then sublimes in crystals in a state of perfect purity. (Wöhler, Ann. Ch. Pharm. c. 376.)

β. From native *Molybdate of lead.*—The mineral finely pounded and freed from carbonates of zinc, iron, and calcium, by digestion in dilute hydrochloric acid, and thoroughly washed by decantation, is heated with 1¼ pt. strong sulphuric acid, with constant stirring, till the sulphuric acid begins to evaporate. It is then allowed to cool, a considerable quantity of water is added, and the insoluble sulphate of lead is filtered off. The filtrate is mixed with nitric acid and evaporated, with constant stirring, in a porcelain basin, till the acid begins to evaporate; the molybdic anhydride then separates as a white powder, which may be freed from phosphoric acid by washing with water, mixed at the last with a few drops of nitric acid.—Or the mineral, after treatment with dilute hydrochloric acid, may be evaporated to dryness with strong hydrochloric acid, the dry residue (containing oxychloride of lead and molybdic anhydride) exhausted with ammonia; the ammoniacal solution crystallised, or evaporated as before with nitric acid; and the residue treated with water. Or again, the mineral is fused with its own weight of calcined cream of tartar; the fused mass is exhausted with water; the aqueous solution exaporated to dryness, after saturation with nitric acid; and the nitrate of potassium is dissolved out of the residue with water: trioxide of molybdenum then remains behind.

Properties.—Trioxide of molybdenum, as usually prepared, forms a white, light, porous mass, which when thrown into water, separates into small thin scales having a silky lustre and glistening in sunshine. Specific gravity = 3·49. At a red heat it melts to a dark yellow liquid, which on cooling forms a straw-yellow mass, breaking up into crystalline scales. By slow cooling of the melted mass, slender needles are obtained belonging to the trimetric system and exhibiting the faces $\infty\breve{P}\infty$, $\infty\breve{P}\frac{3}{2}$, $\frac{1}{3}\bar{P}\infty$ &c. (referred to the prism ∞P, observed by Breithaupt on molybdin). Ratio of secondary axes to principal axis = 1 : 0·3872 : 0·4792 (Nordenskiöld, Pogg. Ann. cxii. 160). In close vessels it bears a strong red heat without volatilising; but in open vessels or in a current of air, it sublimes at its melting point in colourless laminæ.

Decompositions.—1. Molybdic trioxide is reduced:—1. To the metallic state by ignition with *potassium* or *sodium* (with vivid incandescence) or with *charcoal;* also when strongly heated in a stream of *hydrogen.*—2. To molybdous oxide, by digestion with *hydrochloric acid* and *amalgam of potassium*, or *zinc*, or other metal capable of decomposing water.—3. To molybdic oxide, by ignition in combination with ammonia, or by digestion with *hydrochloric acid* and *molybdenum* or *copper;* also, according to Buff (Ann. Ch. Pharm. cx. 257), by subjecting it in the fused state to the action of the *electric current;* the molybdic oxide thus separated unites with the excess of trioxide, forming the compound $MoO^2.2MoO^3$ or Mo^3O^8, which separates in crystalline laminæ and gradually forms a conducting communication between the poles.—4. To the state of blue oxide, by a small quantity of *sulphydric acid*, in presence of water, or on exposure to heat, with separation of sulphur; by *sulphurous acid*, with production of sulphuric acid; by aqueous *hydriodic acid*, with separation of free iodine, and formation of a liquid which at first is green, but afterwards blue; by boiling *hydrochloric acid*, with disengagement of chlorine; by *nitric oxide* in presence of water, with formation of nitrous acid (Kastner, Kastn. Arch. xxvi. 465); by *stannous chloride*, with formation of stannic chloride; also by digestion with water and *metallic molybdenum.*—5. To sulphide of molybdenum, by *sulphydric acid* in excess, in presence of water, or when aided by heat. Molybdic trioxide is not affected by fusion with metallic molybdenum. (Berzelius.)

Combinations. 1. With Water.—Molybdic trioxide is but slightly hygroscopic. It dissolves, according to Bucholz, in 500 parts of cold water, and in a much smaller quantity at a higher temperature: according to Hatchett, it requires 960 parts of hot water. The solution has a faint metallic taste, reddens litmus-paper, yields a red precipitate with ferrocyanide of potassium, but not till one of the stronger acids is added. Graham (Chem. Soc. J. xvii. 326), by dialysing a solution of sodic molybdate mixed with a large excess of hydrochloric acid, has obtained a solution of molybdic acid (containing about 60 per cent. of the quantity present in the original solution), having a yellow colour, astringent to the taste, acid to test-paper, and capable of decomposing carbonates with effervescence. Evaporated to dryness at 100°, it leaves molybdic trioxide in scales like gum or gelatin, and still soluble in water. It does not appear possible to obtain molybdic acid in the solid state.

2. With Acids. The affinity of molybdic acid for other acids is very feeble. After ignition, it is but slightly soluble in a boiling aqueous solution of cream of tartar; before ignition, however, it dissolves in some of the stronger acids, *e.g.* in *boric*, *phosphoric*, *sulphuric*, *nitric*, and *hydrochloric acids*, forming compounds which may be called permolybdic salts. The solutions thus obtained are sometimes colourless, sometimes yellow or brownish. By metallic *zinc* or *tin*, they are first turned blue, then green, and lastly black, molybdous oxide being precipitated; by digestion with *copper*, they become dark red. *Stannous chloride* produces a greenish-blue precipitate, which dissolves in hydrochloric acid, forming a green solution. *Sulphydric acid*, in small quantities, colours them blue; in larger quantities it produces a blackish-brown precipitate (a mixture of disulphide of molybdenum with sulphur, according to Berzelius). *Sulphide of ammonium* behaves in a similar manner to sulphydric acid (Bucholz, Berzelius). *Ferrocyanide of potassium* produces a dense, reddish-brown precipitate, soluble in excess of the reagent, and also in ammonia (Berzelius). *Ferricyanide of potassium* gives a somewhat lighter coloured precipitate, which is likewise soluble in ammonia (H. Rose). *Tincture of galls* throws down a green precipitate. (Smithson.)

Permolybdic Borate. Molybdic trioxide dissolves in boiling aqueous boric acid, and the filtered solution yields by evaporation colourless crystals, decomposible by alcohol into a yellow powder and boric acid. (Berzelius.)

Permolybdic Nitrate. The solution of molybdic trioxide in nitric acid is reddish-brown, has a feebly acid and subsequently bitter, metallic, astringent taste, and gives off nitric acid when evaporated.

Permolybdic Phosphate or *Phosphomolybdic Acid.* Molybdic trioxide digested while still moist with a small quantity of aqueous phosphoric acid, yields a lemon-yellow salt insoluble in water (Berzelius). With a larger proportion of phosphoric acid, this yellow salt dissolves on the application of heat, forming a colourless liquid, which yields by evaporation, a tenacious, uncrystallisable, transparent mass, having a very rough taste, and very soluble in water and in alcohol. The alcoholic solution is yellow, but turns blue on evaporation, and leaves a brown, opaque residue, which redissolves in water, forming a blue solution. (Berzelius; see also Svanberg and Struve, Ann. Ch. Pharm. lxviii. 209, 293.)

The yellow precipitate formed on adding molybdate of ammonium to the solution of a tribasic phosphate (p. 1032) appears to vary in composition according to the circumstances of its formation; at all events the formulæ (all very complicated) assigned to it by different chemists do not agree with one another (see Nutzinger, Jahresb. 1855, p. 274.—Seligsohn, *ibid.* 1856. p. 375.—Eggertz, *ibid.* 1860, p. 620).—[For the modes of applying phosphomolybdic as a test for the alkaloïds, see i. 127.]

Permolybdic Sulphate. By boiling dilute sulphuric acid with an excess of molybdic trioxide, a turbid, milky liquid is obtained, which gelatinises on cooling, and deposits pale yellow flakes of a basic compound, sparingly soluble in water but not in alcohol, though the latter colours it green. (Berzelius.)

A solution of molybdic trioxide (not in excess) in dilute sulphuric acid has a light yellow colour, and dries up to a lemon-yellow crystalline mass, which deliquesces in the air, but is only partially soluble in water (Berzelius). According to Anderson (Berz. Jahresb. xxiii. 161), the solution of molybdic acid in sulphuric acid does not yield crystals on evaporation; but when molybdate of barium is decomposed by excess of dilute sulphuric acid, and the clear solution evaporated over oil of vitriol, crystals are obtained.

Permolybdic Tartrate. The solution of molybdic trioxide in aqueous tartaric acid, yields by evaporation a blue non-crystalline mass, perfectly soluble in water and in alcohol. A boiling solution of acid tartrate of potassium easily dissolves molybdic trioxide, even after ignition. The solution dries up to a gummy mass of *potassio-permolybdic tartrate.* (Berzelius.)

3. With **Bases**, forming the MOLYBDATES. Molybdic trioxide exhibits with most metallic oxides the characters of an anhydrous acid, or anhydride, forming **neutral molybdates** containing $R^2O.MoO^3$ or R^2MoO^4; **acid and double molybdates**, which may be represented by the general formula $R^{2m}Mo^nO^{4n}$, the molecule R^{2m} being made up of two or more metals, including hydrogen; and **anhydro-molybdates**, expressible by the general formula $R^{2n}Mo^nO^{4n}.mMoO^3$, the letters *m* and *n* representing whole numbers. The neutral molybdates of the alkali-metals are easily soluble in water, and are obtained by digesting molybdic anhydride with the aqueous alkalis or alkaline carbonates. They are decomposed by the stronger acids, with precipitation either of a less soluble acid salt, or of molybdic anhydride. Their behaviour with other reagents has been already described (p. 1032). The molybdates of the other metals are insoluble, and are obtained by precipitation. They are colourless unless they contain a coloured base.

Molybdate of Aluminium. White precipitate, insoluble in water.

Molybdates of Ammonium. The *neutral salt*, $(NH^4)^2MoO^4$, is obtained by treating molybdic anhydride in excess with strong aqueous ammonia in a closed vessel, precipitating the solution with alcohol, and drying over quicklime.

Acid salts.—These are obtained by evaporating a solution of molybdic anhydride in excess of ammonia. If the evaporation takes place quickly, a crystalline powder is precipitated, which, according to Svanberg and Struve, is an anhydro-molybdate, $(NH^4)^2O.2MoO^3$ or $(NH^4)^2MoO^4.MoO^3$. It is probable, however, that the salt thus prepared contains 1 at. water, $[(NH^4)^2O.2MoO^3.H^2O]$, in which case it may be regarded as an *ammonio-hydric molybdate*, $\left.\begin{matrix}NH^4\\H\end{matrix}\right\}MoO^4$. A salt having this composition is in fact described by v. Rath (Pogg. Ann. cx. 18) as crystallising in monoclinic prisms, $\infty P \,.\, \infty P3 \,.\, [\infty P\infty] \,.\, \infty P\infty \,.\, -P \,.\, +2P$, and having the ratio of the axes $a : b : c = 0{\cdot}6297 : 1 : 0{\cdot}2936$; the angle of the inclined axes = 91° 12′; and perfectly cleavable parallel to $[\infty P\infty]$.

c. A *tetrammonio-hexhydric-molybdate*, $\left.\begin{matrix}(NH^4)^4\\H^6\end{matrix}\right\}Mo^5O^{20}$, separates from a solution of molybdic anhydride in ammonia, when concentrated to the crystallising point or left to evaporate in the air, in large transparent six-sided prisms. (Svanberg and Struve.)

When a solution of this salt is boiled with *aluminic*, *chromic*, *ferric* or *manganic* *hydrate*, and then evaporated to the crystallising point, double salts are obtained, the composition of which may be represented by that of the aluminic salt, viz.

$$3[(NH^4)^2O.2MoO^3] + \overset{\prime\prime\prime}{Al}{}^2O^3.6MoO^3 + 20H^2O \text{ or } \left.\begin{matrix}(NH^4)^{\prime\prime\prime 3}\\ Al\\ H^6\end{matrix}\right\} Mo^6O^{24}.7H^2O.$$

This salt crystallises in small, white, shining, quadratic plates, less soluble in water than the corresponding potassium-salt (which dissolves in 40·67 pts. water at 17°). The crystals give off 3¼ at. water when exposed to the air, and 3¾ at. more (the remaining water of crystallisation) between 100° and 120°, without losing their lustre; the remaining 3 at. (which are basic) at a higher temperature only; when strongly heated, they yield a yellowish residue of alumina and molybdic anhyride, retaining the form of the original crystals.

The *ammonio-chromic salt* crystallises in small rose-red quadratic plates, which give off 5 at. water at 100° and 2 at. more at 120°, and when heated to redness, leave a mixture of chromic oxide and molybdic anhydride; the *ammonio-ferric salt* forms yellowish-white crystals of the same form, but difficult to obtain pure in any considerable quantity.

The *ammonio-manganic salt*, $5[(NH^4)^2O.2MoO^3] + Mmn^2O^3.6MoO^3 + 12H^2O$, or $\left.\begin{matrix}(NH^4)^5\\ (Mmn)^{\prime\prime\prime}\\ H^8\end{matrix}\right\} Mo^8O^{32}.2H^2O$, is isomorphous with the corresponding potassium-salt (p. 1049); dissolves in 101·7 pts. water at 17°; is permanent in the air; and gives off three-fourths of its total quantity of water at 100°. (Struve.)

Molybdates of Barium. The *monobarytic salt*, $Bba''MoO^4$, is precipitated as a sparingly soluble crystalline powder, on adding chloride of barium to a solution of molybdic acid in excess of ammonia. (Svanberg and Struve.)

Schultze by fusing together 2 pts. molybdate of sodium, 6 pts. chloride of barium, and 2 pts. chloride of sodium, obtained the same salt in distinct quadratic pyramids; with 4 pts. sodic chloride it was obtained as a crystalline powder.

The salts $Bba''H^4Mo^3O^{12}.H^2O$ and $\overset{\prime\prime}{B}ba^2H^6Mo^5O^{20}.3H^2O$ are obtained by precipitating the corresponding potassium- and ammonium-salts with chloride of barium; and by decomposing monobarytic molybdate with dilute nitric acid, an anhydro-salt is formed containing $Bba''MoO^4.8MoO^3.4H^2O$, crystallised in small six-sided prisms, fusible and insoluble in water. (Svanberg and Struve.)

Molybdate of Cadmium, $Ccd''MoO^4$, if obtained in shining yellow laminæ by melting together 2 pts. molybdate of sodium, 7 pts. chloride of cadmium, and 6 pts. common salt. (Schultze.)

Molybdate of Calcium, $Cca''MoO^4$, is obtained by fusing together 2 pts. molybdate of sodium, 6 pts. chloride of calcium, and 4 pts. common salt, in white, well-developed quadratic pyramids. (Schultze.)

Cerous Molybdate is obtained by precipitation, in white flakes insoluble in water, but soluble in several acids. (Berzelius.)

Molybdates of Chromium. Ammonio- and *potassio-chromic molybdates* are obtained, as above described, by dissolving chromic hydrate in the acid molybdates of ammonium and potassium.

Molybdate of Cobalt is obtained in greyish-green indistinct crystals, by fusing 1 pt. molybdate of sodium with 2 pts. chloride of cobalt and 2 pts. common salt. (Schultze.)

Cupric Molybdate. Yellowish-green precipitate sparingly soluble in water, decomposed by acids and by alkalis (Berzelius). Acid molybdate of ammonium added to a boiling solution of cupric sulphate throws down a heavy green amorphous powder, consisting of a basic cupric molybdate, $4Ccu''O.3MoO^3.5H^2O$, or $3Ccu''MoO^4.Ccu''H^2O^2.4H^2O$. By adding molybdate of ammonium in excess to a cold solution of cupric sulphate, an *ammonio-cupric salt* is formed consisting of $Ccu''(NH^4)^2Mo^2O^8.3MoO^3.9H^2O$ or $[Ccu''(NH^4)^2H^6]Mo^5O^{20}.6H^2O$. It is a white-blue crystalline powder which gives off 4 at. water at 100° and 4 at. more at 200°. (Struve.)

Molybdates of Iron. Monoferrous molybdate, $Ffe''MoO^4$, is obtained in dark brown monoclinic prisms by fusing 1 pt. molybdate of sodium with 3 pts. ferrous chloride and 2 pts. common salt (Schultze). Ferrous sulphate added to a solution of potassic molybdate reduces the molybdic acid to a lower stage of oxidation; but if chlorine be passed through the solution at the same time, a bulky precipitate is formed, which, when dried in the air, forms a light yellow powder consisting of $Ffe^2O^3.5MoO^3.16H^2O$ (Struve). A solution of acid molybdate of ammonium mixed with a neutral solution of ferric chloride immediately produces a bulky sulphur-yellow precipitate, which when dried contains $Ffe^2O^3.4MoO^3.7H^2O$. (Steinacker, Jahresb. 1861, p. 238.)

A mineral from Nevada city in California, described by Owen (Jahresb. 1852, p. 887) as a ferric molybdate, is, according to Genth (Sill. Am. J. [2] xxviii. 248), very variable in composition, and appears to be merely a mixture of molybdic ochre and brown hæmatite.

Ammonio-ferric and *Potassio-ferric molybdates* are obtained in the manner already mentioned (p. 1037).

Molybdate of Lead. $Pb^2O.MoO^3 = Ppb''MoO^4$. This salt occurs native as *Wulfenite* or *Yellow Lead ore* (*Gelbbleierz*) in modified square tables and octahedrons belonging to the dimetric system, the most frequent forms being P and P . oP. Length of principal axis = 1·574. Angle P : P in the terminal edges = 99° 40′; in the lateral edges = 131° 35′. Cleavage indistinct parallel to P. It occurs also granularly massive, coarse or fine, firmly coherent. Hardness = 2·75 to 3. Specific gravity = 6·3 to 6·9. Lustre resinous or adamantine. Colour wax-yellow passing into orange-yellow, also siskin- and olive-green, yellowish-grey, greyish-white and brown. Streak white. Subtransparent to subtranslucent. Fracture subconchoïdal. Brittle. When heated, it decrepitates strongly, and assumes a darker colour, disappearing however on cooling, and fuses to a yellow mass. When fused on charcoal before the blowpipe, it sinks into the charcoal, leaving globules of lead, the charcoal at the same time becoming impregnated with molybdenum and molybdide of lead. It dissolves easily in *borax* and in *microcosmic salt*, exhibiting the reactions of molybdenum already mentioned (p. 1032). It dissolves in hot *nitric acid*, with separation of yellowish-white permolybdic nitrate, (p. 1037). Strong *hydrochloric acid* dissolves it, forming a green solution, together with chloride of lead, which separates more completely on addition of alcohol. It dissolves also in caustic *potash*.

Molybdate of lead occurs, with other lead ores, in veins of limestone, at Schwarzenbuch, Bleiberg, and Windish-Kappel, in Carinthia; it is also found at Retzbanya, in Hungary, and at Moldawa in the Bannat, where the crystals are red, and bear considerable resemblance to chromate of lead; in small quantities also at the Southampton lead mine, Massachusetts, and in fine reddish-orange crystals, containing a trace of chromic acid, at Wheatley's lead mine near Phœnixville, Pennsylvania. The specimens from these several localities are nearly pure, the proportion of molybdic anhydride found by analysis varying from 37·65 to 40·5 per cent., and that of lead-oxide from 59·0 to 62·3 per cent., while the formula $Pb^2O.MoO^3$ requires 38·5 per cent. MoO^3 and 61·5 Pb^2O. The Bleiberg mineral contains a small quantity of vanadium.

Molybdate of lead is formed artificially by precipitating nitrate of lead with neutral molybdate of ammonium; also, according to Schulze, by fusing 2 pts. molybdate of sodium with 6 pts. chloride of lead and 4 pts. common salt. As thus prepared, it forms crystals, white, when pure, yellow if they contain a little phosphoric acid. Mixtures, in varying proportions of molybdate of sodium, chromate of potassium, chloride of lead, and common salt, yield crystallised salts, which, when they contain not more than 42 per cent. chromate of lead, are quadratic like those of pure molybdate of lead, but with a deep red colour; with from 42 to 90 per cent. chromate of lead, they are monoclinic and yellow.

A molybdate of lead from Pampluna, in South America, was found by Boussingault (Ann. Ch. Phys. [3] xlv. 325) to contain 73·8 per cent. Pb^2O, 10·0 MoO^3, 2·9 CO^2, 1·3 HCl, 1·3 P^2O^5, 1·2 Cr^2O^3, 1·7 Fe^4O^3, 2·2 Al^4O^3 and 3·7 quartz (= 98·1); he regards it as a basic salt, $3Pb^2O.MoO^3$ or $Ppb^4MoO^4.2Ppb''O$.

Molybdate of Magnesium, $Mmg''MoO^4.5H^2O$, is obtained in distinct crystals by boiling molybdic acid and *magnesia alba* with water, and evaporating the filtrate; it gives off 3 at. water at 100°. (Struve.)

Molybdate of Manganese is obtained as a heavy, white, crystalline powder, containing $Mmn''MoO^4.H^2O$, by treating carbonate of manganese with trimolybdate of potassium or sodium; it gives off its water above 100°, dissolves sparingly in boiling water, and when boiled for some time with the acid molybdate of potassium or sodium, yields double salts (Struve). Schultze, by fusing 1 pt. molybdate of sodium with 3 pts. manganous chloride, and 2 pts. common salt, obtained the anhydrous salt $Mmn''MoO^4$, in large dingy yellow crystals having the aspect of bitter spar, and appearing under the microscope as small monoclinic [?] tablets. Together with this salt there are often formed large red-brown laminæ of indeterminate form.

Ammonio- and *potassio-manganic molybdates* are prepared by boiling the acid molybdates of ammonium and potassium with manganic hydrate (pp. 1037, 1040).

Molybdates of Mercury. On adding mercurous nitrate to a solution of trimolybdate of potassium, a yellowish-white flocculent precipitate is formed, which, if immediately collected on a filter, and washed till the wash-water leaves no residue on evaporation and ignition, consists of *mercurous dimolybdate* or *anhydro-molybdate*, $Hhg^2O.2MoO^3$ or $Hhg^2MoO^4.MoO^3$. It is yellowish-white and non-crystalline, but is converted by prolonged washing, or more quickly by boiling in the mother-liquor, into golden-yellow needle-shaped crystals of *neutral mercurous molybdate*, Hhg^2MoO^4. (Struve.)

Molybdates of Molybdenum. There are several oxides of molybdenum, intermediate in composition between the di- and tri-oxides, which are probably molybdates containing molybdenum as their base. When a solution of molybdate of ammonium is mixed with a solution of molybdic chloride, a blue precipitate is formed having the composition of a molybdic molybdate, $Mo''O^2.4Mo^{vi}O^3$ or Mo^5O^{14}. The precipitate thus formed is, however, a hydrate, which becomes nearly black when ignited. The same blue hydrate is formed by the oxidation of molybdic, or the reduction of permolybdic salts (pp. 1035, 1036). It is very sparingly soluble in sal-ammoniac, somewhat more in water, slightly also in alcohol. The aqueous solution has a dark blue colour, remains unaltered at ordinary temperatures, but bleaches more and more by oxidation when evaporated by heat. A concentrated solution is resolved by alkalis immediately, a dilute solution on warming, into molybdic hydrate and molybdic anhydride.

Another molybdic molybdate, supposed by Berzelius to have the composition $MoO^2.2MoO^3 = Mo^3O^8$, is formed when a mixture of the preceding compound with molybdic chloride is precipitated by ammonia, also when the blue oxide is digested with pulverised molybdenum, or when 2 pts. of the pulverised metal and 1 pt. molybdic trioxide are digested with a large quantity of water in a closed vessel, the colour of the liquid then changing from blue to green. From these solutions pulverised sal-ammoniac throws down the compound as an olive-green precipitate, which redissolves when washed with water. From the product obtained by the first method, water dissolves, first the compound $MoO^2.4MoO^3$, and afterwards molybdic hydrate. (Berzelius.)

Molybdate of Nickel forms as a light apple-green precipitate. Schultze, by fusing molybdate of sodium with chloride of nickel, obtained it in leek-green monoclinic prisms, together with lemon-yellow crystals of indeterminate form.

Molybdates of Potassium.—*a.* The *neutral* or *monomolybdate*, $K^2O.MoO^3$, or K^2MoO^4, is obtained by agitating the trimolybdate with alcoholic potash; it then separates as an oily mass, which, when dried over lime and oil of vitriol, crystallises in four-sided prisms containing $2K^2MoO^4.H^2O$. It is also produced by mixing a solution of molybdate of ammonium with excess of carbonate of potassium, and evaporating to a syrup.

β. When a solution of molybdic acid in carbonate of potassium is mixed with strong nitric or hydrochloric acid, till a slight permanent precipitate appears, the liquid, after a while, yields crystals of a salt containing $4K^2O.9MoO^3.6H^2O$, or $(K^8H^{10})Mo^9O^{36}.H^2O$; and this salt is decomposed by water into the monomolybdate, which dissolves readily, and the trimolybdate, which is sparingly soluble:

$$2(4K^2O.9MoO^3) = 3(K^2O.MoO^3) + 5(K^2O.3MoO^3).$$

The *trimolybdate* dissolves easily in boiling water, and separates as a milky-white precipitate when the solution is quickly cooled; but by slow cooling it is obtained in beautiful silky needles containing $K^2O.3MoO^3.3H^2O$, or $(K^2H^4)Mo^3O^{12}.H^2O$.

Nitric acid added in excess to a solution of molybdic acid in carbonate of potassium, throws down a white precipitate, consisting sometimes of $K^2O.4MoO^3$, sometimes of $K^2O.5MoO^3$, both anhydrous. (Svanberg and Struve.)

Potassio-aluminic Molybdate, $\left.\begin{matrix}K^3\\ All'''\\ H^6\end{matrix}\right\}Mo^6O^{24}.7H^2O$.—This salt, analogous in composition to the ammonio-aluminic molybdate already described (p. 1037), is prepared either by prolonged boiling of a solution of trimolybdate of potassium with aluminic hydrate; or by precipitating a solution of alum with a neutral molybdate, that of magnesium, for example, and boiling the washed precipitate, consisting of aluminic hydrate, sulphate, and molybdate (mixed perhaps with a little potash), with a solution of potassic trimolybdate, and evaporating the filtrate to the crystallising point. It crystallises in groups of small white square tablets, soluble in 40·7 pts. water at 17°; is permanent in air at ordinary temperatures; gives off 6 at. water at 100°; melts when more strongly heated, and solidifies on cooling to a yellowish crystalline mass, very slowly soluble in water and even in acids. (Struve.)

The *potassio-chromic salt* of similar constitution, crystallises in rose-coloured tablets soluble in 38·51 per cent. water at 17°, permanent in the air, giving off 10 at. water at 100°, and behaving at higher temperatures like the aluminic salt. (Struve.)

The *potassio-ferric salt* forms yellowish-white crystals of the same form as the preceding salts; difficult to obtain in any considerable quantity. (Struve.)

The *potassio-manganic salt*, $5K^2O.Mmn^2O^3.16MoO^3.12H^2O$ or $\left.\begin{matrix}K^5\\ Mmn'''\\ H^8\end{matrix}\right\}Mo^8O^{32}.2H^2O$, is prepared, either by boiling manganic hydrate with trimolybdate of potassium, or better, by passing chlorine through a hot solution of potassic trimolybdate, and gradually adding small quantities of manganous sulphate, as long as the solution is thereby rendered darker in colour. The filtered liquid yields the double salt, after cooling or concentration, in shining orange-coloured rhombohedrons, having the angle of their terminal edges = 107° 46′. It dissolves in 384·3 pts. water at 17°, more easily in boiling water, by which however it is partially decomposed. It gives off 9 at. water at 100°, 2 at. more at 160°, acquiring at the same time a darker colour; melts at a higher temperature, and solidifies on cooling into a brownish-red crystalline mass. With nitrate of silver, it forms a precipitate containing molybdic acid, manganic oxide, and silver-oxide, which decomposes during washing. (Struve.)

Molybdates of Silver.—*a. Neutral argentic molybdate*, Ag^2MoO^4, is obtained by precipitating the neutral potassium-salt with nitrate of silver as a yellowish-white, flocculent precipitate, which darkens on exposure to light, dissolves sparingly in water, easily in dilute nitric acid.—*β.* Trimolybdate of potassium forms with nitrate of silver a yellowish-white flocculent precipitate, of somewhat variable composition, but agreeing best with the formula $2Ag^2MoO^4.3MoO^3$. (Svanberg and Struve.)

Argentous molybdate, $Ag^4O.2MoO^3 = Ag^4MoO^7$, is produced by the action of hydrogen gas at ordinary temperatures on the neutral argentic salt; or better, by passing hydrogen gas through a tube having a narrow aperture, into a saturated solution of the argentic salt in moderately strong aqueous ammonia; the reduction then also takes place at ordinary temperatures, but much more quickly at 90° (at higher temperatures some of the silver may be reduced to the metallic state). By the first method it is obtained as an amorphous mass; by the second, as a black, shining, crystalline powder, consisting of regular octahedrons. It is dissolved by nitric acid, with evolution of nitric oxide, and decomposed by potash (not by dilute ammonia) with separation of black argentous oxide. (Wöhler, Ann. Ch. Pharm. cxiv. 119.)

Molybdates of Sodium.—The *neutral* or *disodic molybdate*, $Na^2MoO^4.H^2O$ (commonly called the *monomolybdate*), is obtained by fusing molybdic anhydride with an equivalent quantity of crystallised carbonate of sodium. It is easily soluble in water, and crystallises in small octahedrons, which melt and give off their water at a moderate heat. *Sodio-hydric* molybdate, $NaHMoO^4$ (or *dimolybdate*, $Na^2O.2MoO^3.H^2O$), obtained in a similar manner, crystallises in needles, and dissolves sparingly in cold, readily in boiling water. The *disodio-tetrahydric molybdate*, $Na^2H^4Mo^3O^{12}.5H^2O$ (or *trimolybdate*, $Na^2O.3MoO^3.7H^2O$), is obtained, by adding nitric acid to a solution of molybdic acid in carbonate of sodium, as a bulky white precipitate, more soluble than the corresponding potassium-salt. Nitric acid, added in excess to a solution of molybdate of sodium, throws down nothing but molybdic anhydride. (Svanberg and Struve.)

Trimolybdate of sodium boiled with alumina, chromic oxide, &c., forms double salts analogous to the potassium-salts above described.

Molybdate of Strontium is obtained in well-developed square pyramids by fusing together 1 pt. molybdate of sodium, 2 pts. chloride of strontium and 2 pts. common salt. (Schultze.)

Molybdate of Zinc, $Zn''MoO^4$, is obtained by fusing 2 pts. molybdate of sodium with 3 pts. chloride of zinc and 6 pts. common salt, in white needles, with a tinge of yellow, appearing under the microscope as square prisms, also exhibiting the combination $P . \infty P$; fusible without decomposition before the blowpipe. (Schultze.)

MOLYBDENUM, OXYBROMIDES OF. *Molybdous Oxybromide*, $\overset{''}{Mo}{}^3Br^4O$, is produced by heating molybdous bromide with dilute solutions of caustic alkalis; when treated with hydrochloric, hydriodic and hydrobromic acid, it yields molybdous chlorobromide, &c. (Blomstrand, see p. 1029.)

Permolybdic Oxybromide, $Mo^{vi}Br^2O^2$, is produced by passing bromine vapour over the heated dioxide, or by fusing molybdic trioxide with boric or phosphoric anhydride, and heating the pulverised mass with bromide of potassium:

$$MoO^3 + B^2O^3 + 2KBr = 2KBO^2 + MoBr^2O^2.$$

When quickly sublimed, it forms indistinct crystalline scales; by slow sublimation, more fully developed crystalline plates. It has a yellowish-red colour and fatty lustre, deliquesces in the air, and forms a colourless solution with water. (Blomstrand.)

MOLYBDENUM, OXYCHLORIDES OF. *Molybdous Oxychloride*, $\overset{''}{Mo}{}^3Cl^4O$, is produced in the same manner as the corresponding oxybromide, and reacts in a similar manner with hydrochloric acid, &c. (Blomstrand, p. 1039.)

Permolybdic Oxychlorides. *a.* $Mo^{vi}Cl^2O^2$ or $MoCl^6.2MoO^3$.—Discovered by

Berzelius, first correctly analysed by H. Rose (Pogg. Ann. xl. 399). It is produced in the amorphous state, when any other chlorine-compound of molybdenum is heated in contact with the air, and when the same compounds are exposed to moist air, even at ordinary temperatures (Blomstrand, Jahresb. 1857, p. 193). In the crystalline state it is obtained by the following processes: 1. By passing chlorine over the heated dioxide (Berzelius).—2. By pouring strong sulphuric acid on a mixture of molybdic trioxide and potassic sulphate, evaporating the excess of acid in a retort as completely as possible, then adding chloride of sodium, and heating again, whereupon the oxychloride sublimes; but this process does not yield so pure a product as the first (H. Rose).—3. By repeated sublimation of the brown oxychloride (Blomstrand).—4. By subliming a mixture of this brown compound and the amorphous modification of α (Blomstrand). It forms yellowish-white, delicate, crystalline scales (Berzelius); thin, translucent, nearly square plates of pale-reddish colour, or if obtained by the fourth method, thicker crystals of honey-yellow colour and scarcely translucent (Blomstrand). Tastes sharp and astringent, with sweetish after-taste; volatilises, without fusing, at a heat below redness; and is resolved by water into molybdic and hydrochloric acids, both of which remain dissolved; it is soluble also in alcohol.

A hydrate of the preceding compound, $MoCl^2O^2.H^2O$, which may also be regarded as a *hydrochlorate of molybdic trioxide*, $MoO^3.2HCl$, is obtained by passing hydrochloric acid gas over the trioxide heated to 150°—200°, as a white crystalline, very volatile substance, which is resolved by heat into hydrochloric acid and trioxide of molybdenum, but may be volatilised without decomposition in hydrochloric acid gas. It dissolves easily in water, but the solution when evaporated leaves nothing but molybdic trioxide (Debray, Ann. Ch. Pharm. cviii. 250). The permolybdic sulphate, nitrate, &c., described at p. 1037, are perhaps analogous in constitution to the compound just mentioned, but they have not been analysed.

β. $Mo^{vi}Cl^4O$ or $2MoCl^6.MoO^3$?. This is a green, easily fusible oxychloride, obtained by passing chlorine over an intimate mixture of molybdic oxide and charcoal (or even imperfectly reduced molybdenum still containing oxygen) heated by a common spirit-lamp. The bulky amorphous oxychloride which first forms is to be removed, and the sublimate which forms when the vapour has acquired a permanent blood-red colour is to be collected. It is indistinctly crystallised in dark green tufts; if formed at a somewhat stronger heat, in light green metallic-shining scales. It melts and volatilises below 100°, forming a dark red-brown vapour, and is decomposed by water, yielding hydrochloric acid and blue oxide of molybdenum. Hence, and from the results of analysis, Blomstrand regards it as $Mo^9Cl^{32}O^8$ or $2(MoCl^4.2MoCl^6) + MoO^2.2MoO^3$, but observes that the analytical numbers do not differ much from those required by the simpler formula above given.

γ. $Mo^4Cl^{10}O^5 = (MoCl^4.MoCl^6).(MoO^2.MoO^3)$. This is a brown, easily fusible substance, produced by the action of chlorine on a mixture of charcoal and sesquioxide of molybdenum (formed from the trioxide by the prolonged action of hydrogen at a red-heat, or by the reducing action of zinc in the wet way). The latter part of the product is collected apart and purified by fractional sublimation in an atmosphere of hydrogen. When very slowly sublimed, it forms large brown or black-brown crystals. (Blomstrand.)

δ. $Mo^2Cl^6O^3 = MoCl^6.MoO^3$. Produced, though only occasionally and in small quantity, by the action of chlorine at a moderate heat on a mixture of molybdic oxide and charcoal, accompanying the green oxychloride β, which is formed towards the latter part of the process. It may be freed from the latter, and from any other compounds that may be present, by its inferior volatility. It forms well-defined prismatic crystals of a dark violet colour by reflected, ruby-red by transmitted light; it volatilises with difficulty, but without previous fusion. Water first dissolves it with slight rise of temperature, and then throws down a white precipitate, soluble in a larger quantity of water.

MOLYBDENUM, PHOSPHIDE OF. MoP.—A mixture of 1 pt. yellow trioxide of molybdenum containing phosphoric acid, and 2 pts. fused phosphoric acid containing lime, is exposed for an hour in a charcoal crucible to the heat of a very strong coke fire, whereby a grey blistered mass is formed, consisting of small metallic shining crystals of phosphide of molybdenum, mixed with calcic phosphate, and having its cavities lined with the same crystals.

Phosphide of molybdenum forms a powder of specific gravity 6·167. The crystals conduct electricity. It is very difficult to fuse; oxidises gradually in the *air* without burning, but with incandescence on melting *nitre*. By hot *nitric acid* it is converted into phosphoric and molybdic acids, and dissolved. When gently heated in *chlorine gas*, it is converted, without visible combustion, into chloride of molybdenum and chloride of phosphorus. In contact with *zinc* it eliminates hydrogen from *hydrochloric acid*, and on addition of a *copper-salt*, reduces copper on its surface. (Wöhler and Rautenberg, Ann. Ch. Pharm. cix. 374.)

MOLYBDENUM, SULPHIDES OF. Molybdenum unites with sulphur in three proportions, forming the compounds MoS^2, MoS^3, and MoS^4. The last two are sulphur-acids. Our knowledge of these sulphides and their salts is almost wholly due to the researches of Berzelius.

Disulphide or Molybdic Sulphide. MoS^2.—This compound occurs native as *Molybdenite* (*Molybdänglanz*, *Wasserblei*), generally in crystallo-laminar masses, more rarely in tabular crystals, ∞P . oP, belonging to the hexagonal system, cleavable parallel to oP. Hardness = 1 to 1·5; easily impressed by the nail. Specific gravity = 4·44 to 4·8. The mineral has a strong metallic lustre and pure lead-grey colour; streak similar, but slightly inclined to green; it forms a grey trace on paper, and a greenish trace on porcelain. It is opaque, sectile, and almost malleable; laminæ highly flexible and elastic.

Molybdenite is of frequent occurrence in primitive rocks, being sometimes found in metalliferous veins, especially of magnetic iron ore and tin ores. It is found in Cornwall, at Caldbeck Fell in Cumberland, in Saxony, Bohemia, Sweden, Norway, and Greenland, and at numerous localities in the United States. It occurs nearly pure, but according to Svanberg and Struve, generally contains a small quantity of phosphoric acid (or phosphorus), a fact which must be borne in mind when the mineral is used for the preparation of molybdate of ammonium.

Disulphide of molybdenum is produced artificially by heating either of the higher sulphides, also by igniting the trioxide with sulphur. The artificial sulphide is a black shining powder.

The disulphide heated in closed vessels, sustains a high temperature without fusing or undergoing any change, and according to H. Rose, is not decomposed by ignition in dry hydrogen gas. When heated in the air, it is converted into molybdic anhydride, with evolution of sulphurous anhydride. Before the blowpipe on *charcoal* it gives off sulphurous anhydride, covering the charcoal with a yellowish-white incrustation; but it burns with great difficulty, and the combustion is but imperfect. On *platinum wire* it colours the outer blowpipe flame green. It colours a bead of *borax* mixed with *nitre*, dark brown in the inner flame, and light brown in the outer.

It decomposes *vapour of water* at a red heat slightly, but at a higher temperature with greater facility. It detonates with *nitre*, forming a molybdate of potassium; dissolves readily in warm *nitromuriatic acid*, producing molybdic and sulphuric acids, is easily oxidised by *nitric acid;* dissolves in boiling oil of vitriol with evolution of anhydride, and forms a blue solution.

Trisulphide. *Sulphomolybdic acid.* MoS^3.—This compound, the analogue of the trioxide, is formed by decomposing that compound with sulphydric acid, viz. (1) by passing the gas into a concentrated solution of an alkaline molybdate and precipitating with an acid; or (2) by adding sulphide of ammonium to the solution and then hydrochloric acid, both in excess. The whole of the molybdenum is then precipitated as trisulphide, which settles down quickly, and must be rapidly washed on a filter with water containing sulphydric and hydrochloric acids, to prevent oxidation. As thus obtained it is a black-brown powder which makes a dark brown streak on porcelain. When heated it gives off sulphur, and is converted into the disulphide. It dissolves, but not readily, in caustic alkalis, more easily at the boiling heat, undergoing partial decomposition at the same time. It is most easily dissolved by *alkaline monosulphides* and *sulphydrates*, forming sulphur-salts called sulphomolybdates; the alkaline disulphides do not dissolve it.

The sulphomolybdates are the analogues of the molybdates, most of them being constituted according to the formula $R^2S.MoS^3$ or R^2MoS^4. There are also a few containing 2 or 3 at. of the sulphur-acid. The sulphomolybdates of the alkali-metals, alkaline earth-metals, and magnesium, are soluble in water; the rest are insoluble. The alkali-metal salts are obtained by passing sulphydric acid gas into concentrated solutions of the corresponding molybdates; the insoluble salts by precipitating a neutral oxygen-salt of the metal with a soluble sulphomolybdate.

The aqueous solutions of neutral sulphomolybdates have a fine red colour when pure, changing to brown, however, if they contain a small quantity of iron or an excess of the sulphur acid. During evaporation, they emit a constant odour of sulphydric acid. When exposed to the air, they remain unaltered, if they contain an excess of the sulphur-acid; in the contrary case, the solutions—and likewise the dry salts—are rapidly oxidised, the sulphide of the alkali-metal being converted into hyposulphite, while the trisulphide of molybdenum is partly precipitated as such, partly converted into trioxide and blue oxide of molybdenum. The sulphomolybdates are decomposed by acids, with evolution of sulphydric acid and precipitation of molybdic trisulphide. When heated to redness, they yield molybdous sulphide and a disulphide of the base, or give off 1 at. sulphur.

Sulphomolybdate of Ammonium, $(NH^4)^2MoS^4$, separates from a concentrated aqueous solution mixed with alcohol in cinnabar-coloured scales, becoming dark brown on exposure to the air. The aqueous solution, if left to evaporate, yields at the edges a number of crystals which are green by reflected light, while in the middle it dries up to a black amorphous mass. The salt is sparingly soluble in alcohol.

Bodenstatt (J. pr. Chem. lxxviii. 186; Jahresb. 1859, p. 163), by passing sulphydric acid gas to supersaturation into a solution of impure molybdic acid in hydrochloric acid, mixed with a large quantity of sal-ammoniac and previously supersaturated with ammonia, obtained deep red crystals of a *sulphoxymolybdate*, $(NH^4)^2MoO^2S^2$.

Sulphomolybdates of Barium.—The *neutral salt*, $Bba''MoS^4$, is obtained, as a dark red amorphous mass, from the mother-liquor of the following salt. The *trisulphomolybdate*, $Bba''S.3MoS^3$ or $Bba''MoS^4.2MoS^3$, is obtained by boiling sulphide of barium with an excess of molybdic trisulphide, and separates from the hot filtrate on cooling, in small yellow shining crystals, which, when laid on paper, crumble to a shining powder of the same colour. They give off water, and turn red when heated, and are decomposed by dilute, but not by concentrated hydrochloric acid.

The *cadmium-salt* is a dark brown precipitate insoluble in water.

An acid *calcium-salt*, probably $Cca''MoS^4.2MoS^3$, is obtained like the corresponding barium-salt, and crystallises in short, shining, vermillion-coloured, needle-shaped crystals, permanent in air even at 100°; hydrochloric acid blackens them by separating the sulphide of molybdenum. The mother-liquor of this salt, when evaporated, leaves the *neutral calcium-salt* in the form of a dark red varnish.

Cerous sulphomolybdate is a dark grey precipitate. On adding an alkaline sulphomolybdate to the solution of a ceric salt, only a slight precipitate is formed, but ammonia throws down from the resulting yellow solution a basic salt in the form of a brown gummy mass.

The *chromic salt* is a dark brown precipitate, which turns green in drying. The *cobalt-* and *copper-salts*, are dark brown precipitates, the former soluble in sulphide of potassium.

The *gold-salt* (*auric*) is soluble in water, whence it separates after some time as a dark brown powder, becoming black when dry.

Iron-salts.—The *ferrous* salt is soluble in water, forming a wine-red solution, which becomes darker and nearly black on exposure to the air; when evaporated in a shallow vessel, together with sulphomolybdate of potassium, it ultimately separates from the latter as a black jelly, which, as well as the dilute solution, deposits a pale red-yellow powder by spontaneous evaporation. The *ferric salt* is a dark red precipitate which dissolves, with black colour, in excess of sulphide of potassium, but generally separates again after 24 hours. When dry it is black and yields a brown powder.

The *lead-salt* is a black precipitate, which when dry, forms a lead-grey, metallic-shining streak on paper.

Magnesium-salts.—By boiling molybdic trisulphide with sulphydrate of magnesium, and cooling, a dark brown powder is obtained, consisting of an *acid sulphomolybdate of magnesium*. The supernatant liquid contains the neutral-salt and dries up to a dark red varnish.

Manganese-salts.—By digesting sulphide of manganese in excess with molybdic trisulphide, a brownish-yellow liquid is obtained, which dries up to a transparent varnish. Ammonia throws down from the solution a red basic salt, which is decomposed by a larger quantity of ammonia. Sulphide of manganese digested with excess of molybdic trisulphide forms an insoluble compound.

Mercury-salts.—*Mercurous sulphomolybdate* is a nearly black, the *mercuric salt* a light brown precipitate. The *nickel-salt* resembles the cobalt-salt. The *platinum-salt* is a dark brown precipitate, black after drying.

Potassium-salts.—*a.* The *neutral salt*, K^2MoS^4, is produced by heating a mixture of potassic carbonate, sulphur, charcoal powder and excess of molybdic trisulphide in a crucible, gently at first, afterwards very strongly. The black unfused mass yields with water, after cooling, a dark red opaque solution. A similar solution is obtained by saturating a solution of potassic molybdate with sulphydric acid. When evaporated in a cylindrical vessel at 40°, it yields four and six-sided prisms, with dihedral summits, which are dark red by transmitted, but of a fine dark green colour by reflected light, and yield a dark red powder, becoming green and shining by pressure. Alcohol added to the red aqueous solution, throws down a cinnabar-coloured powder, and the mixed liquid deposits scales of the same colour which acquire a green metallic lustre by drying. The salt heated in an atmosphere of hydrogen is only partially decomposed into disulphide of potassium and molybdous sulphide.—*β.* Another salt containing a larger proportion of molybdic trisulphide, is precipitated as a brown-yellow powder, when the solution of the neutral salt is mixed with a quantity of acetic acid sufficient to give it an acid reaction. It is black after drying, and dissolves easily in boiling, slowly in cold water, forming a yellow solution. A solution of the neutral salt, mixed with a small quantity of any other acid, becomes darker, in consequence of the formation of this compound, but does not yield a precipitate.

A compound of *sulphomolybdate* and *nitrate of potassium* is obtained when a solution of equal parts of the two salts is left to evaporate. It then separates in green metallic-shining scales, very much like sulphomolybdate of potassium, which burn away like gunpowder when heated.

The *silver-salt* resembles the lead-salt in colour and streak.

Sodium-salts.—The *neutral salt* forms small dark red granular crystals, much more soluble in alcohol than the potassium-salt. It is almost completely reduced by ignition in hydrogen gas. There is also an *acid* sulphomolybdate of sodium, much less soluble than the neutral salt, and resembling the corresponding potassium-salt in all its properties.

The *strontium-salts* resemble the barium-salts.

The *uranium-* and *zinc*-salts are dark brown precipitates; the *stannous* salt is a black precipitate; the *stannic* salt, a translucent brown precipitate becoming grey-brown when dry.

Tetrasulphide of Molybdenum. *Persulphomolybdic acid*, MoS^4.—This sulphide is thrown down by hydrochloric acid from the solutions of alkaline persulphomolybdates, as a flocculent translucent precipitate of a fine dark red colour, shrinking together when dry, into a coarse-grained mass, possessing a dark green metallic lustre, and yielding a dark red powder when triturated with water. It is insoluble in water and in acids. When heated in a retort, it gives off water and a small quantity of sulphurous anhydride, then a large quantity of sulphur, and leaves disulphide of molybdenum.

Persulphomolybdates. Tetrasulphide of molybdenum unites with basic metallic sulphides, forming salts represented by the formula $R^2S.MoS^4 = R^2MoS^5$. Most of them are dark red and retain their colour unaltered when dry. The persulphomolybdates of the alkali-metals are soluble in water, and their solutions yield with acids a precipitate of molybdic tetrasulphide.

The *ammonium-salt* is obtained by drenching moist molybdic tetrasulphide with sulphydrate of ammonium, to which a little caustic ammonia may be advantageously added. A yellow powder is then formed, which becomes dark red when dry, is insoluble in alkaline liquids, sparingly soluble in cold, easily in hot water.

Barium-salt.—Yellow or red precipitate, insoluble in water, and not decomposed by dilute hydrochloric acid. The *calcium-salt* is precipitated after some time by alcohol from a mixture of the potassium-salt with chloride of calcium, as a cinnabar-coloured powder slightly soluble in water.

The *copper-salt* is a precipitate dark coloured at first, but becoming red inclining to brown after it is collected. The *gold-salt* (auric) is a brown precipitate which turns yellow and decomposes in drying, and when heated in contact with the air, burns, gives off sulphurous anhydride, assumes a golden-yellow colour, and when very strongly heated, yields a sublimate of molybdic trioxide.

Iron-salt.—Red precipitate formed on adding the potassium-salt to an excess of a ferrous salt.

The *lithium-salt* resembles the potassium-salt. The *magnesium-salt* is an insoluble red precipitate.—The *mercurous salt* is a dark almost brown precipitate.

Potassium-salts.—When sulphomolybdate of potassium is boiled with molybdic trisulphide (such a mixture is obtained by decomposing an acid molybdate of potassium with sulphydric acid), the boiling being continued for several hours in a retort, a large quantity of sulphydric acid is given off with the watery vapours, and a copious precipitate is formed. On collecting the precipitate after cooling on a filter and washing till the wash-water gives a dark red flocculent precipitate with hydrochloric acid, a residue is obtained from which water extracts persulphomolybdate of potassium, leaving disulphide of molybdenum behind. The resulting solution is red, and generally yields the salt on evaporation in the form of a red mass, having the consistence of an extract. On one occasion, however, Berzelius observed the salt to separate from the boiled mixture on cooling, in small ruby-coloured crystalline granules which could be separated from the rest of the precipitate by levigation. They appeared under the microscope as transversely striated rectangular scales; were insoluble in cold water, hydrochloric acid, and potash, but soluble in hot water. At a low red heat, they decrepitated, gave off water, a small quantity of sulphur, and sulphydric acid, after which water extracted sulphide of potassium from them, leaving disulphide of molybdenum.

When a dilute solution of sulphomolybdate of potassium containing an excess of molydic trisulphide is exposed to a heat of 60°—80°, it becomes turbid and gradually yields a lighter coloured deposit of persulphomolybdate of potassium, which, after drying, forms a yellow coherent mass consisting of small crystalline particles having a silky lustre. The same mass is obtained by drenching molybdic tetrasulphide with sulphydrate of potassium. It is insoluble in cold, but soluble in hot water.

Persulphomolybdate of silver is a dark brown precipitate, black when collected.

The *sodium-* and *strontium-salts* resemble the potassium- and barium-salts respectively.

Tin-salts.—The *stannous salt* is obtained from stannous chloride by double decomposition, as a dark brown precipitate. If the mixture be left for several days in an open vessel, the stannic salt is formed and the supernatant liquid becomes red.—The *stannic salt* is only partially precipitated, the rest remaining dissolved with the same colour.

MOLYBDIN. Syn. with molybdic ochre, or native trioxide of molybdenum.

MOMORDICA. According to Lepine (J. Pharm. [3] xl. 16), *Momordica charantia* yields a solid fat melting at 65°.—On the amount of elaterin contained in the fruit of *Momordica Elaterium* at different seasons, see Walz (N. Jahrb. Pharm. xi. 21).

MOMORDICIN. Syn. with ELATERIN (ii. 373).

MONARDA, OIL OF. The essential oil of an American Labiate plant, the *Monarda punctata*. It easily separates into a liquid oil and a camphor. The oil or essence is a yellowish-red liquid, having an odour of thyme, becoming light yellow after rectification with water, boiling at 224°, and easily resinising by oxidation. The camphor or stearoptene, when purified by pressure and distillation, forms shining crystals, melting at 48° and solidifying again at 38°. Its composition, according to Arppe's analysis, is $C^{10}H^{14}O$; that of the oil separated from the stearoptene appears to be $(C^{10}H^{14})^2O$. The crystals absorb 2 or 3 per cent. hydrochloric acid gas. (Arppe, Ann. Ch. Pharm. lviii. 41; Handw. d. Chem. v. 377.)

MONAZITE. *Edwardsite, Mengite, Eremite.*—A phosphate of cerium and lanthanum, also containing thorinum according to some authorities, occurring in monoclinic prisms, usually small and flattened. Ratio of axes, $a : b : c : = 1{\cdot}0265 : 1 : 0{\cdot}94715$. Angle of b and $c = 76°\ 14'$. Observed planes, $\infty P\infty$, $[\infty P\infty]$, $+P\infty$, $-P\infty$, $+P$, $-P$, ∞P, $[\infty P2]$, and others. Cleavage basal, very distinct and brilliant. Hardness = 5 to 5·5. Specific gravity = 4·9 to 5·25. The crystals have a brownish-red, hyacinth-red, or yellowish-brown colour, and resinous lustre; they are substransparent to subtranslucent and rather brittle. The mineral is infusible before the blowpipe; dissolves slowly in borax, forming a bead which is yellowish-green or yellowish-red while hot, colourless when cold.

Analysis.—*a.* From Slatoust in the Ural; Brooke's *Mengite* (Kersten, Pogg. Ann. xlvii. 385).—*b.* The same (Hermann, J. pr. Chem. xxxiii. 90).—*c.* Rio Chico, Antioquia, in New Granada:

P^2O^5.	Th^2O.	Ce^2O.	La^2O.	Ca^2O.	Mg^2O.	Mn^2O.	SnO^2.		
28·50	17·95	24·78	23·40	1·68	. .	1·86	2·10	=	100·27*
28·05	. .	37·36	27·41	1·46	0·80	. .	1·75	=	96·83
29·1	. .	46·4	24·5	. .	. .	. .	. .	=	100·00

The presence of thorinum in monazite has been confirmed by Berzelius and Wöhler. Hermann, on the contrary, denies it, and is of opinion that a basic sulphate of cerium formed in the analyses has been mistaken for sulphate of thorinum. The analytical results may be represented by the formula $(Ce;\ La)^3PO^4$ or $(Ce;\ La;\ Th)^3PO^4$; but new analyses are required to fix the formula with certainty.

Monazite was first obtained from Slatoust. It occurs also at Norwich and Watertown in Connecticut; at Yorktown, Chester County, New York; and near Crowder's Mountain, North Carolina.

MONAZITOÏD. The name given by Hermann (J. pr. Chem. xl. 20) to a variety of monazite from the Ural, distinguished by its brown colour, higher specific grvaity (= 5·281), and by the presence of tantalum. Hermann found in it 17·94 per cent. P^2O^5, 49·35 Ce^2O, 21·30 La^2O, 1·50 Ca^2O, 1·36 H^2O, and 6·27 TaO^2. It gives off a small quantity of chlorine when treated with hydrochloric acid, and dissolves, leaving a considerable yellow residue.

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* With traces of titanic acid and potash.

MONESIN. A compound resembling saponin, contained in an extractive substance called *Monesia*, which appears to be obtained from the bark of *Chrysophyllum glycyphæum*, a Brazilian plant of the sapotaceous order. (Desrone, Henry and Payen, Ann. Ch. Pharm. xxxvii. 352.)

MONHEIMITE. Syn. with KAPNITE (p. 445).

MONO-COMPOUNDS. This term is applied to compounds containing 1 at. of the element specified, *e.g.*, $C^2H^3ClO^2$, *monochloracetic acid*, $C^6H^5.H^2.N$, *monophenylamine*, &c.

MONOPHANE. Syn. with EPISTILBITE (ii. 491).

MONOTROPA. According to F. L. Winckler (N. Jahrb. Pharm. viii. 322), the herb of *Monotropa hypopitys*, gathered when the flowers are almost fully expanded, yields by distillation with water, a volatile oil identical with that of *Gaultheria procumbens* (ii. 825). The residue of the distillation contained an acid.

MONRADITE. A magnesio-ferrous silicate from Bergen in Norway, where it occurs massive granular; also foliated, with one distinct and another imperfect cleavage inclined at 130°. Hardness = 6 nearly. Specific gravity = 3·2673. It has a pale yellow colour inclining to red, and a strong vitreous lustre. Contains 56·17 per cent. silica, 31·63 magnesia, 8·56 ferrous oxide, and 4·04 water (= 100·40, agreeing nearly with the formula $4(\frac{4}{5}Mg.\frac{1}{5}Fe)^2SiO^3.H^2O$. (Erdmann, K. Vet. Acad. Handl. 1842; Dana, ii. 280.)

MONROLITE. Syn. with KYANITE (p. 449).

MONTANINE. An alkaloïd said by Van Mons to exist in *China montana*, the bark of *Exostemma floribundum*. Winckler was not able to find it.

MONTICELLITE. A variety of chrysolite (i. 958).

MONTMORILLONITE. A rose-red, fragile, argillaceous substance found at Montmorillon near Confolens in Charente, and near St. Jean de Colle in Dordogne. Contains 50·04 per cent. silica, 20·16 alumina, 0·68 ferric oxide, 1·46 lime, 0·23 magnesia, 1·27 potash, and 26·0 water. (Damour, Bull. Soc. geol. de France [2] iv. 464.)

MOONSTONE. A variety of translucent felspar from Ceylon. (See FELSPAR, ii. 620.)

MORDANTS. See DYEING (ii. 352).

MORDENITE. A fibrous zeolite from the trap of the Bay of Fundy, Nova Scotia, the name being derived from Morden, a village near which it is found. It occurs in small concretions or geodes of white, yellowish or pinkish colour, and strong silky lustre, weathering dull; cleaves readily in directions parallel to the fibres; is translucent on the edges. Hardness a little above 5. Specific gravity = 2·08. Rather brittle. Before the blowpipe it fuses at a strong heat to a glassy bead, without intumescence; with hydrochloric acid it does not gelatinise but yields slimy silica. Contains (mean of analyses) 68·40 per cent. silica, 12·77 alumina, 3·46 lime, 2·35 soda, and 13·02 water (= 100), agreeing very nearly with the formula, $(\frac{1}{3}Na.\frac{2}{3}Ca)^2O.Al^4O^3.9SiO^2.6H^2O$, which is reducible to that of a metasilicate, $M^2(R^4)^{vi}H^{16}Si^9O^{27}.H^2O$. (How, Chem. Soc. J. xvii. 104.)

MORIC ACID. *Morin.* (R. Wagner, J. pr. Chem. li. 82; Hlasiwetz and Pfaundler, *ibid.* xc. 445.)—An acid existing in old fustic (*Morus tinctoria*), and deposited as a calcium-salt, together with morintannic acid, from an infusion of the wood on cooling. To extract it, the deposit (sometimes called *morin*) is treated several times with boiling alcohol; the alcoholic liquor is diluted with six times its bulk of water, which precipitates the morate of calcium in the form of a yellow crystalline powder, while the whole of the morintannic acid remains dissolved. The calcium-salt is then dissolved in boiling alcohol, the calcium precipitated by oxalic acid, and the moric acid is separated from the hot filtrate by water, purified by re-solution in alcohol and re-precipitation by water, and finally dried over the water-bath out of contact with air (Wagner). Hlasiwetz and Pfaundler treat the deposit above mentioned twice with boiling water, after pressing it, and thereby obtain a solution of morintannic acid (p. 1049), and a residue consisting of crude moric acid and nitrate of calcium. This residue is heated with water and a little hydrochloric acid (to decompose the calcium-salt), then washed with water and dissolved in hot alcohol. The filtrate mixed with two-thirds of its volume of hot water, deposits the greater part of the moric acid in yellow crystals, which may be purified by solution in weak alcohol (using filters free from lime and iron), and formation of a small quantity of lead-sulphide in the solution, to carry down resinous matters.

Moric acid is a white crystalline powder, which gradually turns yellow in contact with the air. According to Hlasiwetz and Pfaundler, it crystallises in needles several lines long, mostly grouped in tufts. It is very sparingly soluble in *water*, requiring 4000 pts. at 20° and 1060 pts. at 100° to dissolve it; very soluble in *alcohol* and in *ether* (Wagner), sparingly soluble in *ether*, insoluble in *sulphide of carbon* (Hlasiwetz and Pfaundler). The solutions have a deep yellow colour, and slight acid reaction. Dried at 120°, it contains, according to Wagner, 55·2 per cent. carbon, and 3·2 hydrogen, numbers which may be represented by the formula $C^{18}H^{14}O^{9}.H^{2}O$. This composition differs but little from that of morintannic acid; indeed Delffs (Zeitschr. Chem. Pharm. 1862, p. 143) concludes, from his own experiments, that Wagner's moric acid is nothing but morintannic acid contaminated with colouring matter. On the other hand, Wagner (Chem. Centr. 1862, p. 399) still maintains the distinctness of moric from morintannic acid, inasmuch as the former is colourless, much less soluble in water than the latter, and reacts differently with alkalis. The difference between the two acids is further established by the experiments of Hlasiwetz and Pfaundler.

Moric acid bears a rather high temperature without decomposing. At 300° it blackens and gives off a considerable quantity of carbonic anhydride, together with a yellow oil which partly concretes on cooling, and consists of a mixture of phenol and oxyphenic acid (pyrocatechin). It dissolves in weak acids without coloration; in strong *sulphuric acid* with brown-yellow colour, and is precipitated by water in its original state. The sulphuric acid solution decomposes when heated, giving off sulphurous anhydride and phenol. Strong *nitric acid* converts moric acid into oxypicric acid. With *caustic alkalis* and their *carbonates*, moric acid form solutions of a fine yellow colour: paper impregnated with it affords a delicate test for free alkalis. The solution does not precipitate *gelatin*, but it stains *animal skin* yellow. *Ferric chloride* colours the solution garnet-red (Wagner), deep olive-green (Hlasiwetz and Pfaundler). A solution of moric acid boiled with *cupric sulphate* or *acetate*, after addition of potash, yields a precipitate of cuprous oxide. From an ammoniacal solution of *silver-nitrate*, it immediately reduces metallic silver.

Morate of Barium is produced by boiling the acid with recently precipitated carbonate of barium: the resulting solution when evaporated yields the salt in the form of a red-brown powder, apparently containing $3C^{18}H^{12}BaO^{9}.C^{18}H^{14}O^{9}.H^{2}O$. The *calcium-salt* exists ready formed in fustic, and is deposited from its alcoholic solution in sulphur-yellow crystals which apparently contain $C^{18}H^{12}CaO^{9}.H^{2}O$, and give off their water at 100°. (Wagner.)

MORINDIN. A substance obtained by Anderson (Ed. Phil. Trans. xvi. [6] 435; Ann. Ch. Pharm. lxxi. 216) from the root of *Morinda citrifolia*, the "Al" root of the Hindoos, frequently used as a dye-stuff in the Madras Presidency. When this root is exhausted with boiling alcohol, the first decoctions deposit brown flocks of morindin contaminated with a red colouring matter, but the last portions yield it in small radiated yellow crystals. The whole is purified by repeated crystallisation from dilute alcohol slightly acidulated with hydrochloric acid.

Morindin forms crystals having a fine yellow colour and satin lustre. It is sparingly soluble in cold, more soluble in boiling *alcohol*, especially when dilute; in *absolute alcohol* it is less soluble, and quite insoluble in *ether*. Cold *water* dissolves it but sparingly, sufficiently however to acquire a yellow colour; boiling water dissolves it easily, and deposits it on cooling as a gelatinous mass, destitute of crystalline structure.

Morindin dried at 100° gives by analysis 55·4 per cent. carbon and 5·1 hydrogen, whence Anderson deduces the formula $C^{28}H^{15}O^{15}$ or $C^{28}H^{30}O^{15}$ (requiring 55·4 per cent. C, 4·9 H, and 39·6 O). Rochleder regards it as identical with the ruberythric acid (54·5 C, 5·2 H, 40·3 O), which he obtained from madder.

Morindin dissolves in *alkalis*, forming orange-red solutions. Strong *sulphuric acid* colours it deep purple, or violet in thin layers; the solution, if diluted with water after 24 hours, deposits yellow flocks of unaltered substance, quite insoluble in cold water, and forming with ammonia, not an orange-red, but a violet solution.

Nitric acid of specific gravity 1·38 dissolves morindin slowly in the cold, acquiring a deep red colour; on heating the liquid, a brisk reaction takes place; the solution boiled with nitric acid and neutralised with ammonia does not precipitate calcium-salts.

Basic acetate of lead precipitates morindin in crimson flocks, which are not very stable and cannot be washed without loss of colouring matter. Solutions of *baryta*, *strontia* and *lime* form bulky precipitates sparingly soluble in water.

Ferric chloride produces a brown coloration, but no precipitate. An ammoniacal solution of morindin forms with *alum* a reddish liquid, and with *ferric chloride* a precipitate having the colour of ferric oxide.

Morindin heated in a close vessel melts and boils, giving off orange-coloured vapours, which condense in long slender yellowish-red needles of alizarin (Anderson's *morindone*).

When powdered morinda-root is boiled with moderately dilute *sulphuric acid*, as in the ordinary garancin process, its morindin is converted into alizarin; but the large quantity of brown matter produced at the same time, greatly diminishes the value of the dye-stuff obtained, as it renders the colours dull and the whites difficult to clear. The "Al" root is therefore never likely to compete successfully with madder, at least in Europe; nevertheless it affords the best known source of pure alizarin, this substance, when prepared from it, being quite free from purpurin, which, as is well known, is very difficult to separate completely from the alizarin prepared from ordinary madder. (Stenhouse, Chem. Soc. J. xvii. 334.)

MORINDONE. See the last article.

MORINGIC ACID. $C^{15}H^{28}O^2$.—An oily acid, homologous with oleic acid, obtained, together with stearic, palmitic and benic acids, by the saponification of oil of ben (*Moringa aptera*). It is colourless or faintly yellow, has a density of 0·908, a mawkish taste, which irritates the throat, and a faint odour. It reddens litmus paper; is very soluble in common alcohol, even in the cold; solidifies at the freezing point of water; is decomposed by heating with sulphuric acid. Walter found in it 75·0 per cent. carbon, and 11·7 hydrogen, the above formula requiring 74·9 C, 11·8 H, and 13·3 O. (*Gerhardt's Traité de Chim. org.* ii. 882.)

MORINTANNIC ACID. *Maclurin.* $C^{13}H^{10}O^6$. (R. Wagner, J. pr. Chem. li. 82. Hlasiwetz and Pfaundler, *ibid.* xc. 445; Jahresb. 1863, p. 594.)—A variety of tannic acid which constitutes the chief colouring matter of old fustic (*Morus tinctoria*, or according to Hlasiwetz and Pfaundler, *Maclura tinctoria*). It forms a large portion of the deposits found in the interior of faggots of that wood, and may be obtained by treating these deposits with boiling water and leaving the extract to cool. The acid is then deposited in the form of powder and may be purified by crystallising it several times from pure water, and dissolving the crystalline deposit in water slightly acidulated with hydrochloric acid, to separate a resinous substance, and filtering the solution when it is no longer turbid. (Wagner.)

A strongly concentrated aqueous decoction of fustic left to itself for some days yields an abundant crystalline deposit, which when pressed and twice boiled with water yields a residue consisting of crude moric acid and morate of calcium, and a solution of morintannic acid, which deposits a portion of the acid on evaporation, the rest on addition of hydrochloric acid. It may be freed from resinous impurities, first by crystallisation from water acidulated with hydrochloric acid, and finally by adding to the solution a small quantity of acetate of lead, and precipitating with sulphydric acid in presence of free acetic acid. (Hlasiwetz and Pfaundler.)

Morintannic acid is deposited from its solution as a light yellow crystalline powder, composed of microscopic prisms. It dissolves in 64 pts. of cold, and 2·14 pts. of boiling *water*, the solution having a slight acid reaction, and sweetish astringent taste; easily also in *alcohol, wood-spirit, and ether*; but is insoluble in oil of turpentine and in fixed oils. The ethereal solution is greenish by reflected and brown by transmitted light. (Wagner.)

The composition of morintannic acid is shown by the following analyses and calculations:

At 130°—140°.			
	Calculation.	Hlasiwetz and Pfaundler.	
C^{13}	59·54	59·36	59·25
H^{10}	3·81	4·13	4·18
O^6	36·65	36·51	36·57
$C^{13}H^{10}O^6$	100·00	100·00	100·00

At 100°.			
	Calculation.	Wagner. *mean.*	Delffs.
C^{13}	55·71	55·17	54·1
H^{12}	4·29	4·41	4·4
O^7	40·00	40·42	41·5
$C^{13}H^{10}O^6.H^2O$	100·00	100·00	100·0

Delffs regards the compound dried at 100° as identical with moric acid; but as already observed (p. 1047), the difference between the two acids may be considered as completely established by the recent researches of Hlasiwetz and Pfaundler.

Morintannic acid melts at 200°, blackens and gives off water and acid vapours at 250°, and undergoes complete decomposition at 270°, yielding a large quantity of carbonic anhydride, and an oily distillate which partly solidifies on cooling, and leaving a bulky cinder. The distilled oil is a mixture of phenol and pyrocatechin. (Wagner.)

The aqueous solution of morintannic acid is not precipitated by hydrochloric, sulphuric, phosphoric or arsenic acid, but completely by *gelatin* and softened *animal bladder*.

Morintannic acid dissolves in cold strong *sulphuric acid*, forming a yellow solution from which it is precipitated by water; on heating the solution, it blackens and gives off sulphurous anhydride and phenol. The solution in cold sulphuric acid, if left to itself for some days, yields a brick-red deposit of rufimoric acid. This acid is also deposited after a while from the solution of morintannic acid in boiling dilute *hydrochloric acid.* By boiling concentrated hydrochloric acid, and by oxidising agents, morintannic acid is decomposed, giving off the odour of phenol. With *peroxide of manganese* and *sulphuric acid*, it gives off a large quantity of carbonic anhydride, together with formic acid. Strong *nitric acid* converts it into styphnic (oxypicric) acid. *Chromic acid* decomposes it easily and completely. *Chlorine* passed into its aqueous solution throws down yellow resinous flocks. (Wagner.)

The acid mixed with a solution of 3 pts. *hydrate of potassium* and evaporated in a silver dish till it has become pasty is resolved into phloroglucin and protocatechuic acid. (Hlasiwetz and Pfaundler):

$$\underset{\text{Morintannic acid.}}{C^{13}H^{10}O^{6}} + H^2O = \underset{\text{Phloroglucin.}}{C^6H^6O^3} + \underset{\text{Protocatechuic acid.}}{C^7H^6O^4}$$

Morintannates. Morintannic acid unites directly with caustic alkalis and decomposes the alkaline and earthy carbonates when boiled with them; the solutions of the alkaline morintannates are yellow, but quickly turn brown or black in contact with the air, so that these salts cannot be obtained pure in the solid state. A solution of the acid forms a greenish precipitate with *ferroso-ferric sulphate*, yellow with *acetate of lead*, brown with *potassio-antimonic tartrate*, yellowish-brown with *cupric sulphate*, yellowish-red with *stannous chloride*, yellow and flocculent with *platinic chloride.* It does not immediately precipitate a solution of *alum*, but on adding carbonate of potassium, a yellow lake is thrown down.

A moderately concentrated solution of morintannic acid mixed at the boiling heat with a dilute solution of *neutral lead-acetate*, and quickly filtered, deposits small, yellow laminar crystals containing, when dried at 110°, which temperature they sustain without alteration, 33·09 per cent. carbon, 2·00 hydrogen, and 45·76 lead-oxide, agreeing with the formula $C^{13}H^8PbO^6.PbHO$, which requires 32·84 C, 2·10 H, and 46·00 Pb^2O (Hlasiwetz and Pfaundler). Wagner found in the lead-salt dried at 100°, 32·01 per cent. C, 2·17 H, and 44·27 Pb^2O, which agrees nearly with the formula $C^{13}HPbO^6.PbHO^6.\frac{1}{2}H^2O$.

MOROXITE. A greenish-blue variety of apatite, found at Arendal in Norway, and Pargas in Finland.

MOROXYLIC ACID. A volatile crystalline acid, said by Klaproth to exist as a calcium-salt in the stems of the mulberry tree (*Morus alba*). Landerer found the same calcium-salt in the so-called *Lachrymæ Mori*, which exude from mulberry stems. (Handw. d. Chem. v. 142.)

MORPHETINE. A product of the oxidation of morphine (p. 1052).

MORPHINE, or **MORPHIA.** $C^{17}H^{19}NO^3$.—This alkaloid, the most important of the opium-bases, was known in an impure state, as *Magisterium opii*, in the seventeenth century; but it was not obtained as a well-defined organic base till 1816, when Sertürner published a series of important researches upon it (Gilb. Ann. iv. 61; lvii. 192; lix. 50). It has been further examined by Robiquet (Ann. Ch. Phys. [2] v. 275; li. 232); Pelletier and Caventou (*ibid.* xii. 122); Dumas and Pelletier (*ibid.* xxiv. 182); Lassaigne (*ibid.* xxv. 102); Dublanc (*ibid.* xxvii. 84); Liebig (*ibid.* xlvii. 105; Ann. Ch. Pharm. xxvi. 41); Merck (Ann. Ch. Pharm. xviii. 79; xxi. 202; xxiv. 46); Regnault (Ann. Ch. Phys. [2] lxviii. 131); Laurent (*ibid.* [3] xix. 361); Lefort (J. Pharm. [3] xl. 97); and Guibourt (*ibid.* xli. 97, 177). Good Smyrna opium generally contains from 10 to 15 per cent. morphine. Egyptian opium from 5·8 to 6·6 per cent.; East Indian from 5·3 to 7·7 per cent.

Preparation.—1. Opium is exhausted with cold water; the extract after evaporation to a syrup at a gentle heat, is heated while yet warm with a large excess of carbonate of sodium as long as ammonia continues to escape; the resulting precipitate is collected after twenty-four hours, and washed with cold water; and when the wash-water is no longer coloured, the precipitate is treated with alcohol of 85 per cent., again dried, and exhausted in the cold with very dilute acetic acid, care being taken not to add too much acid at once, and to wait till each portion is neutralised before adding more. The solution is then filtered, decolorised with animal charcoal, and precipitated by ammonia, care being taken to avoid an excess; and the precipitate, after being well-washed, is dissolved in boiling alcohol. The liquid on cooling deposits crystals of morphine, and an additional quantity may be obtained by concentrating the mother-liquors. (Merck.)

2. Twenty pts. of opium cut in slices are boiled in sixty pts. water for half an hour, or until all the slices are opened out; the liquid is then strained, and the residue is squeezed and again twice treated with fresh water in the same way. The united extracts are boiled down to half their bulk, then stirred into a boiling lime-lye composed of 3 pts. slaked lime and 40 pts. water; the liquid is boiled for a quarter of an hour,

and then strained; and the calcareous residue is pressed and again twice boiled in 50 pts. water. The whole of the calcareous liquors are now boiled down to 40 pts. and mixed at boiling heat with 2 pts. sal-ammoniac; the heat is kept up for an hour, or as long as ammonia is given off; the liquid is then allowed to cool; and after eight days the morphine, which separates in the form of brown granules, is collected: the mother-liquor yields another crop if further boiled down and left to itself. The product may be purified by washing in cold water, solution in hydrochloric acid, repeated boiling with excess of milk of lime, and precipitation with sal-ammoniac. (Mohr, Ann. Ch. Pharm. xxxv. 120.)

3. The process most generally employed is that of Robertson, modified by Robiquet and Gregory (Ann. Ch. Pharm. v. 87; vii. 261).—Opium is macerated in water of 38°, till all the soluble principles are extracted; the solution is evaporated with carbonate of calcium, which neutralises the free acids; and when the liquid is sufficiently concentrated, chloride of calcium is added, whereby a precipitate of meconate of calcium is formed, which carries down with it a considerable quantity of colouring matter. The opium bases remain in the solution as hydrochlorates, and the liquid, when again concentrated, first deposits more meconate of calcium, and afterwards crystals of hydrochlorate of morphine mixed with hydrochlorate of codeine. These salts are easily purified by repeated crystallisation, with addition of animal charcoal.

The two hydrochlorates are next dissolved in water and treated with ammonia, which precipitates the morphine, leaving the codeine dissolved. The morphine is finally purified by crystallisation from alcohol.

Morphine prepared by either of the preceding processes is often contaminated with narcotine, from which however it may be freed by either of the following processes:—1. By digestion in ether, which dissolves narcotine much more easily than morphine.—2. By dissolving the mixed bases in hydrochloric acid, evaporating to the crystallising point, and pressing the crystals, which consist entirely of hydrochlorate of morphine, the narcotine-salt remaining in the uncrystallisable mother-liquor.—3. By mixing the hydrochloric acid solution with common salt, which renders the liquid milky, and throws down the narcotine after some days in crystalline agglomerations; the morphine may then be precipitated by ammonia.—4. By pouring a weak solution of caustic potash into the dilute solution of the hydrochlorates; the morphine then dissolves in a slight excess of potash, while the narcotine is deposited as a curdy precipitate, which may be separated by filtration.

For a full account of the various methods used for the preparation and purification of morphine, see *Gmelin's Handbook*, xvi. 416–423.

Properties.—Morphine crystallises in colourless transparent prisms usually very short, belonging to the trimetric system. Observed combination: $\infty P . \infty \breve{P}\infty . \breve{P}\infty$. Angle $\infty P : \infty P = 127° 30'$; $\infty P : \infty \breve{P}\infty = 116° 20'$; $\breve{P}\infty : \infty \breve{P}\infty = 132° 20'$; $\breve{P}\infty : \breve{P}\infty = 95° 20'$. Cleavage parallel to $\infty \breve{P}\infty$. It is inodorous but has a persistently bitter taste, and is extremely poisonous, exerting a strong narcotic action. In small doses it is much used in medicine as a sedative.

Morphine is but very slightly soluble in cold *water*; boiling water dissolves about $\frac{1}{50}$ of it, depositing the greater part of it in the crystalline form as it cools. Cold *alcohol* dissolves but little of it; boiling alcohol a larger quantity. It is insoluble in *ether*, and may thus be easily separated from narcotine, which is dissolved by ether. Morphine is likewise insoluble in *volatile oils*. Aqueous *alkalis*, even *lime-water*, dissolve it readily; *ammonia*, however, but sparingly.

Morphine turns the plane of polarisation of a luminous ray to the left. In the state of concentrated solution in water acidulated with hydrochloric acid, its molecular rotatory power is expressed by $[\alpha] = -88{\cdot}04$. It has likewise about the same amount of rotatory power when dissolved in alcohol.

The crystals of morphine melt when heated, giving off 5·94 per cent. (= 1 at.) water of crystallisation; at a high temperature they become carbonised.

The composition of morphine dried at 120° is expressed by the formula $C^{17}H^{19}NO^{3}$, as seen from the following results of analysis:

	Calculation.		Liebig.*		Regnault.†			Will.‡	Laurent.§	
C^{17}	204	71·58	71·35	71·38	71·87	71·41	71·66	71·40	71·63	71·59
H^{19}	19	6·66	6·69	6·77	6·86	6·84	6·86	6·72	6·58	6·66
N	14	4·91	4·99	. .	5·01					
O^{3}	48	16·85	16·97							
	285	100·00	100·00							

The base called pseudomorphine or phormine, occasionally, found by Pelletier in the aqueous extract of opium containing a large quantity of narcotine, and the metamorphine of Wittstein, found on one occasion only in the residue of the preparation of opium-tincture, were probably nothing but impure morphine. (See *Gmelin's Handbook*, xvi. 440.)

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* Ann. Ch. Pharm. xxvi. 41.

† Ann. Ch. Phys. lxviii. 131.

‡ *Ibid.* xxvi. 44.

§ *Ibid.* [3] xix. 369.

Reactions.—Morphine and its salts are very sensitive to the action of oxidising agents. 1. *Iodic acid* is reduced by morphine either free or combined, the liquid turning brown and emitting an odour of iodine. This reaction will indicate the presence of 1 pt. of morphine in 7000 pts. of liquid (Serullas). *Periodic acid* acts in the same manner. *Ammonia* deepens the colour of a solution of iodic acid and morphine (J. Lefert, J. Pharm. [3] xl. 97). When solid morphine or a morphine-salt is moistened with a solution of 1 pt. iodic acid in 15 pts. water, and a solution of 1 pt. *starch* in 400 pts. water is added, a blue colour is produced, by which $\frac{1}{300}$th of a grain may be detected; if a drop of the starch-solution be previously evaporated with the morphine, the reaction will suffice for the detection of $\frac{1}{10,000}$th of a grain. If a layer of very dilute ammonia be poured upon a solution of morphine mixed with iodic acid and starch, then, even if only $\frac{1}{20,000}$ pt. of morphine is present, two coloured rings will be formed at the surface of contact, the upper being blue, the lower brown; in more dilute solutions only the brown ring is produced. Other substances capable of reducing iodic acid may likewise produce the blue ring, but not the brown ring at the same time. (A. Dupré, Chem. News, viii. 267; Jahresb. 1863, p. 704.)

2. Morphine and its salts slowly reduce *nitrate of silver*.

3. *Chloride of gold* colours them blue, from reduction of the metal.

4. They reduce *permanganate of potassium*, which acquires a green colour

5. *Ferric salts* impart to morphine and its solutions a blue colour, which however is not permanent, and is destroyed by excess of acid, by heat, or by contact with alcohol. This reaction is characteristic of morphine (Robinet). A solution of morphine in sulphuric acid previously heated is coloured deep red by ferric chloride, the colour changing after a while to dirty green. (Husemann, Ann. Ch. Pharm. cxxviii. 305.)

6. When sulphate of morphine mixed with dilute sulphuric acid is boiled with *peroxide of lead*, till the liquid is no longer precipitated by ammonia, the excess of sulphuric acid then removed by carbonate of lead, and the lead by sulphuretted hydrogen, the filtered liquid yields on evaporation a brown amorphous slightly bitter substance (*morphetine*), which reddens litmus, is soluble in water, sparingly soluble in strong alcohol, acquires a darker colour by contact with alkalis, and is not precipitated by acetate of lead. By continued action of the peroxide of lead, it is converted into a yellow deliquescent acid body.

7. *Nitric acid* communicates to morphine an orange-red colour gradually changing to yellow. In this reaction, an acid body is produced which when boiled with potash gives off a volatile oil. (Anderson, Ann. Ch. Pharm. lxxv. 80.)

8. Warm dilute *sulphuric acid* converts morphine into sulphomorphide.

9. Morphine dissolved in strong sulphuric acid containing a little *nitric acid* forms a violet-red solution (J. Erdmann, Ann. Ch. Pharm. cxx. 88). According to A. Husemann (*ibid.* cxxviii. 305), this reaction may be rendered much more certain and delicate by first dissolving the base in strong sulphuric acid, in the proportion of 0·002 to 0·004 grm. to 6 or 8 drops of the acid, and then adding a drop of nitric acid, whereupon, if the morphine-solution has been recently prepared, a rose-colour is produced, changing after a few seconds to yellow, then to greenish, and finally to brown. If a small quantity of water be added to the solution of the morphine in sulphuric acid, so that the mixture becomes hot, the colouring produced by the subsequent addition of nitric acid is of a much deeper carmine-red, and much more durable. If the solution be heated for a few minutes to 100°—150°, the addition of a drop of nitric acid produces, after cooling, a splendid deep violet colour, which gradually disappears from the centre outwards, passing through blood-red. If the temperature be raised above 150°, the liquid acquires of itself at a certain moment, a violet-rose colour; at still higher temperatures, a dirty green colour is produced. On adding a drop of nitric acid, after cooling, the liquid immediately turns red, without passing through violet. A solution of morphine in sulphuric acid, left to itself for 12 to 24 hours at ordinary temperatures, behaves as if it had been heated to 100°—150°.

Hypochlorite of sodium, *chlorine-water*, and *chlorate of potassium* exhibit with morphine the same reactions as nitric acid.

With regard to the sensibility of these reactions, Husemann finds that $\frac{1}{5}$th of a milligramme of morphine is sufficient to produce a very bright carmine colour; $\frac{1}{50}$th mgr. gives a very distinct reaction, and $\frac{1}{100}$th mgr. still gives a perceptible tint after half a minute.

10. When *chlorine* is passed into water containing morphine in suspension, the morphine first acquires an orange colour, then dissolves completely; and if the passage of the chlorine be continued, the liquid turns yellow, and deposits flakes partly soluble in alcohol. (Pelletier.)

11. *Iodine* unites with morphine, forming the so-called iodomorphine (p. 1056).

Morphine heated to 200° with excess of *hydrate of potassium*, yields an alkaline distillate containing methylamine.

12. Morphine heated with the *iodides of methyl* and *ethyl*, yields hydriodate of methyl-morphine or of ethyl-morphine.

To detect the presence of morphine when mixed with animal matter, the substance is mixed with *alumina*, dried between 100° and 110°, then well pulverised and macerated in cold water acidulated with acetic acid. The solution treated with ammonia, deposits morphine, which may then be recognised by the characters above described, especially by its reactions with iodic acid, ferric salts, and nitric acid.

Estimation of Morphine in Opium.—15 grms. of opium cut in pieces are triturated with 60 grms. alcohol of 71 per cent.; the solution is strained through linen; and the residue, after being pressed, is again treated in the same way with 40 grms. alcohol. The alcoholic tincture mixed with 4 grms. of aqueous ammonia yields in 12 hours crystals of morphine and narcotine, which are collected, washed several times with water, and stirred up in the water; the crystals of morphine then sink to the bottom, while those of narcotine, being lighter, remain longer suspended and may be separated by decantation (Guillermond, J. Pharm. [3] xvi. 17). Riegel (Jahrb. pr. Pharm. xxiii. 292) removes the narcotine precipitated together with the morphine, by washing with ether or with chloroform. According to Reveil and Guibourt, the quantity of alcohol employed by Guillermond is not sufficient for the exhaustion of the opium, and 12 hours is not time enough for complete crystallisation. Guibourt therefore treats dry powdered opium, or the aqueous extract of opium, with alcohol, either warm or cold, allowing it in either case to stand in the cold for 24 hours, to permit the separation of the resin, the wax, and a portion of the narcotine. The tincture is drawn off with a pipette, the residue washed with alcohol, and the entire liquid precipitated by a slight excess of ammonia. After evaporation of the excess of ammonia, the morphine is allowed to crystallise out completely, then collected and washed with alcohol of 50 per cent., afterwards with alcohol of 40 per cent., and finally with ether. The extract prepared with cold water from 20 to 30 grms. of opium may also be redissolved in cold water; the solution precipitated by ammonia; and the precipitate collected after 36 hours, washed with cold water, then with alcohol of 40 or 50 per cent., and crystallised from boiling alcohol of 85 per cent. (Guibourt.)

F. F. Mayer (Am. J. Pharm. xxxv. 28) has given a volumetric process for estimating morphine and other alkaloïds founded on their precipitability by *potassio-mercuric iodide*. The standard solution contains 13·546 grms. ($\frac{1}{20}$ at.) mercuric chloride and 49·8 grms. iodide of potassium in a litre; it is to be added to the solution to be tested (and not the contrary), and gives a perceptible precipitate with 1 pt. of morphine in 2500 pts. water. The formation of the precipitate is not interfered with by extractive matters, but is prevented by alcohol, ammonia, and acetic acid; to obtain greater accuracy, the excess of the precipitant may be estimated by a standard silver-solution.

On the estimation of morphine, see further:—Fordos (Compt. rend. xliv. 1256; Kopp's Jahresb. 1857, 603); Meurein (J. Pharm. [3] xxiii. 176 and 262); L. Kieffer (Ann. Ch. Pharm. ciii. 271); A. Petit (J. Pharm. [3] xliii. 45); on an older process by Guillermond, see J. Pharm. xiv. 436.

On the detection and identification of morphine in cases of poisoning, see Lassaigne (Ann. Ch. Phys. [2] xxv. 102); Mermer (J. Chim. xxiii. 12); Stas (J. Pharm. [3] xxii. 281); Flandin (Compt. rend. xxxvi. 517); Otto (Ann. Ch. Pharm. c. 46); v. Uslar and J. Erdmann (Ann. Ch. Pharm. cxx. 121); J. Erdmann (Ann. (Ch. Pharm. cxxii. 360); Helvig, *Das Mikroscop in der Toxicologie*, Maintz, 1864, p. 6; also the article, ALKALOÏDS, in this Dictionary, i. 126.

Salts of Morphine.—Morphine dissolves easily even in dilute acids, forming perfectly neutral salts. It decomposes certain salts of lead, iron, copper, and mercury, combining with their acids. Most morphine-salts are crystallisable, inodorous, bitter, and very poisonous; they are soluble in water and in common alcohol, insoluble in ether, and in amylic alcohol. The solutions exhibit the reactions above described for morphine. According to Lassaigne and Feneulle, they deposit in the circuit of the voltaic battery, needles of morphine at the negative, and the acid at the positive pole. Their aqueous solutions mixed with *ammonia*, *potash*, *soda*, *baryta*, *lime*, or *magnesia* deposit morphine as a crystalline powder soluble in excess of the precipitant, except in the case of magnesia, difficultly soluble in excess of ammonia. According to Anderson (J. Pharm. [3] xiii. 143), the precipitate formed by ammonia is composed of microscopic rhombohedral crystals. Morphine-salts are precipitated by the *neutral carbonates of the alkali-metals*, and the precipitate is not soluble in excess. The *acid carbonates of the alkali-metals* precipitate only a portion of the morphine from neutral morphine-salts; and do not form any precipitate in cold acid solutions. *Tartaric acid* prevents the precipitation of morphine by the acid carbonates of the alkali-metals. (Oppermann, Compt. rend. xxi. 210.)

With *fluosilicic alcohol* (a saturated alcoholic solution of fluoride of silicium) morphine-salts yield a crystalline precipitate; with *phosphomolybdic* acid (p. 1037), a pale yellow flocculent precipitate; they are also precipitated by *phosphotungstic acid* (a mixture of sodic tungstate and phosphoric acid), and by *phosphantimonic acid* (prepared by dropping pentachloride of antimony into aqueous phosphoric acid), not, however, when the solution is diluted 1000 times. (F. Schultze.)

Acetate of Morphine crystallises by spontaneous evaporation in tufts of needles very soluble in water, less soluble in alcohol. Its solution when evaporated by heat, is partly decomposed, giving off acetic acid and depositing crystals of morphine; by rapid evaporation, however, a varnish-like residue is obtained.

Aspartate of Morphine is a gummy mass containing shining crystals, very soluble in water.

Bromomercurate.—Resembles the iodomercurate (p. 1055) and is obtained in a similar manner. (Groves.)

Carbonate.—Morphine dissolves in water strongly charged with carbonic acid under pressure; and the solution cooled to a low temperature deposits carbonate of morphine in shortened prisms soluble in 4 pts. water, and decomposed by heat. Alkaline carbonates added to solutions of morphine throw down the free base.

Chlorate of Morphine forms long slender needles which decompose suddenly when heated, swelling up and carbonising.

Chlorhydrate or *Hydrochlorate of Morphine*, $C^{17}H^{19}NO^3.HCl.3H^2O$, crystallises in silky fibres, soluble in 20 pts. of cold water, in 1 pt. boiling water and still more soluble in alcohol.

The *chloromercurate*, $C^{17}H^{19}NO^3.HCl.2Hhg''Cl^2$, separates as a white crystalline precipitate, on mixing the solutions of its component salts, and the filtered liquid deposits, after a while, tufts of silky crystals, having the same composition. It is very sparingly soluble in water, alcohol and ether at ordinary temperatures, more soluble in boiling alcohol, which deposits it in the crystalline form. Hydrochloric acid dissolves it easily and deposits it by spontaneous evaporation in large crystals.

The *chloroplatinate*, $C^{17}H^{19}NO^3.HCl.PtCl^2$, is obtained as a yellow curdy precipitate; a certain quantity, however, remains dissolved and may be crystallised by evaporation at a gentle heat.

Croconate of Morphine is a dark yellow uncrystallisable bitter mass, soluble in water and in alcohol.

Cynoplatinate of Morphine, $C^{17}H^{19}NO^3.HCy.PtCy$.—Cyanide of platinum and potassium throws down from the aqueous solution of acetate of morphine, an amorphous curdy precipitate which soon becomes crystalline, causing the liquid to solidify into a brilliant white mass. It forms shining globules and funnel-shaped depressed discs consisting of small microscopic needles having a silky lustre when dry; becomes dark-yellow when heated and white again on cooling; melts partially at 150° to a brownish-yellow mass, and when further heated, swells up, gives off cyanogen, and burns with a sooty flame. It does not give off any water of crystallisation at 125°. (Schwartzenbach, Chem. Centr. 1860, p. 304.)

Cyanurate of Morphine forms tufts of long needles mixed with crystals of cyanuric acid, even when morphine is present in excess. It is decomposed by recrystallisation, with formation of a white amorphous mass.

Fluorhydrate or *Hydrofluate of Morphine* forms long colourless prisms sparingly soluble in water, insoluble in alcohol and ether.

Formate.—Small bitter prisms fusible and easily soluble in water.

Gallotannate.—Morphine-salts form with gallotannic acid, or tincture of galls, a white precipitate sparingly soluble in water, freely in acetic acid, gallic acid, and mineral acids, soluble also in alcohol.

Hippurate.—Transparent amorphous mass.

Hydroferricyanate.—Aqueous ferricyanide of potassium added to aqueous hydrochlorate of morphine forms, after a while, a crystalline easily decomposible precipitate (Dollfus); according to Neubauer, on the other hand, no precipitate is formed.—*Hydroferrocyanate.*—Hydroferrocyanic acid throws down from an alcoholic solution of morphine, after long standing, small, white, easily decomposible needles. (Dollfus.)

Iodhydrate or *Hydriodate*, $C^{17}H^{19}NO^3.HI.\frac{3}{2}H^2O$?—On mixing the solutions of 1 pt. iodide of potassium and 2 pts. acetate of morphine, small shining prisms are obtained, moderately soluble in water, and containing 28·8 per. cent. iodine. (Winckler.)

Iodomercurates.—Iodomercurate of potassium throws down from aqueous sulphate or hydrochlorate of morphine, a pulverulent precipitate, which soon becomes gelatinous, and is insoluble in hydrochloric acid (v. Planta, Delffs). When morphine, mercuric chloride, and iodide of potassium are brought together in aqueous solution, a double salt, $C^{17}H^{19}NO^3.HhgI^3$ [or $C^{17}NH^{19}O^3.HI.Hhg''I^2$?] is precipitated, sparingly soluble in water, more soluble in alcohol. It is crystallisable, free from water of crystallisation, not decomposed by dilute acids, even on boiling, or on addition of iodide of potassium; decomposed by caustic alkalis. (Groves, Chem. Soc. J. xi. 97.)

Kinate of Morphine is a transparent gum exhibiting traces of crystallisation.

Meconate of Morphine is uncrystallisable, very soluble in water and in alcohol; reddens ferric salts. This salt is contained in aqueous extract of opium.

Mellitate. $C^{17}H^{19}NO^3.C^4H^2O^4$.—The solution of morphine in hot concentrated aqueous mellitic acid soon deposits white, microscopic, needle-shaped crystals, which give off 2 per cent. of their weight at 110°. They are rather more soluble in cold than in hot water, freely in aqueous ammonia and potash, not in alcohol or in ether (Karmrodt, Ann. Ch. Pharm. lxxxi. 171). A *dibasic mellitate* appears to be formed, as a brown amorphous brittle mass, when cold aqueous mellitic acid is saturated with morphine, and the solution is evaporated. (Karmrodt.)

Nitrate of Morphine forms stellate rays soluble in $1\frac{1}{2}$ pt. water.

Pectate.—Recently precipitated pectic acid dissolves morphine, even in the cold, forming a thick gum which, after dilution with water, is thickened again by acids. (Braconnot.)

Phosphates.—Two phosphates of morphine appear to exist, the neutral salt crystallising in cubes, the acid salt in tufts. Phosphate of sodium added to solutions of morphine-salts, forms a crystalline precipitate very soluble in hydrochloric acid.

Picrate.—Picric acid forms with morphine-salts a sulphur-yellow pulverulent precipitate (v. Planta); no precipitate with the acetate. (Merck.)

Pyrotartrate.—Fissured gum, soluble in water and in alcohol. (Arppe.)

Rhodizonate.—Hyacinth-red; soluble, with reddish colour, in water and in alcohol. (Heller.)

Sulphates.—The *neutral salt* $(C^{17}H^{19}NO^3)^2.H^2SO^4.10H^2O$, crystallises in tufts of colourless prisms, very soluble in water and having a silky lustre. They give off 11·87 per cent. (= 10 at.) water at 130°. There appears also to exist an *acid* sulphate of morphine, which is obtained by supersaturating the preceding salt with sulphuric acid, evaporating to dryness, and removing the excess of acid with ether.

When morphine is dissolved in dilute sulphuric acid, the solution evaporated till it begins to decompose, and cold water then poured into it, a substance called sulphomorphide is precipitated, having a constitution similar to that of an amide—that is to say, it may be regarded as produced from sulphate of morphine by elimination of water:

$$\underset{\text{Sulphate of morphine.}}{(C^{17}H^{19}NO^3)^2H^2SO^4} \quad - \quad 2H^2O \quad = \quad \underset{\text{Sulphomorphide.}}{C^{34}H^{36}N^2O^8S.}$$

Sulphomorphide recently prepared is white and amorphous, but soon turns green even in sealed tubes. It dissolves in dilute acid and alkaline liquids. Strong acids and alkalis decompose it, forming a brown substance.

Sulphocyanate, $C^{17}H^{19}NO^3.CyHS$.—An alcoholic solution of morphine saturated with moderately concentrated sulphocyanic acid yields small, shining, limpid needles which melt at 100°.

Neutral solutions of morphine are not precipitated by sulphocyanate of potassium.

Tartrates. *a. Neutral,* $C^{17}H^{19}NO^3.C^4H^6O^6.3H^2O$.—When a solution of cream of tartar is neutralised with morphine, cream of tartar crystallises out first, then nodules of the morphine-salt, which must be removed in time, so as to keep them separate from the neutral tartrate of potassium which afterwards crystallises out. The salt may also be obtained by slow evaporation of an aqueous solution of tartaric acid neutralised with morphine. It forms nodular groups of crystals consisting of closely aggregated needles; effloresces on the surface at 20°; loses on the average 6·54 per cent. water at 130° (3 at. = 6·8 per cent.), no more at 145°. Exhibits crystal-electricity (ii. 411) when heated to 130° or 140°, and retains it for an hour after cooling. Soluble in alcohol. The easily formed aqueous solution is not precipitated by caustic alkalis, alkaline carbonates, chloride of calcium, or ammonio-chloride of calcium. (Arppe, J. pr. Chem. iii. 332.)

β. Acid salt, $C^{17}H^{19}NO^3.C^4H^6O^6.\frac{1}{2}H^2O$.—Obtained by mixing the solution of the neutral salt with as much tartaric acid as it already contains. Crystallises by spontaneous evaporation in tufts of long rectangular flattened prisms. The air-dried salt gives off 1·99 per cent. ($\frac{1}{2}$ at.) water at 140°.

Urate of Morphine is obtained by boiling uric acid and morphine with *water*, and crystallises on cooling from a solution saturated at the boiling heat, in short brownish prisms which decompose when recrystallised. (Elderhorst.)

Valerate of Morphine forms fine large crystals having a fatty lustre and smelling strongly of valerianic acid. The crystals belong to the trimetric system, and are always hemihedral. Observed combination $\infty P \,.\, \infty P \infty \,.\, \check{P} \infty \,.\, \frac{P}{2}$. Angles measured approximately, $\infty P : \infty P = 100°$; $\check{P} : \check{P} \infty = 125° 47'$; $\check{P} \infty : \frac{P}{2} = 148° 28'$; $\frac{P}{2} : \infty P = 130°$. (Pasteur, Ann. Ch. Phys. [3] xxxviii. 455.)

Derivatives of Morphine.

IODOMORPHINE, $4C^{17}H^{19}NO^{3}.3I^{2}$ (?).—A mixture of equal pts. of iodine and morphine dissolves completely at the boiling heat, forming a brown liquid, which by spontaneous evaporation deposits this compound in the form of a brown-red substance, the mother-liquor retaining hydriodate of morphine. The same compound is obtained by heating a solution of sulphate of morphine with iodine. It dissolves in acid and alkaline liquids when heated therein. It gives by analysis 35·34 per cent. iodine, the formula requiring 39·87 per cent.

Iodomorphine triturated with metallic mercury and a little alcohol gives up part of its iodine to the mercury, and is converted into a yellow amorphous mass, insoluble in cold water, sparingly soluble in boiling water, moderately soluble in alcohol, very soluble in alkaline liquids, insoluble in acids. Treated with nitrate of silver it yields a large quantity of iodide of silver. It melts when heated, giving off ammonia, without any trace of iodine. (Pelletier, Ann. Ch. Phys. lxiii. 185.)

METHYL AND ETHYL-MORPHINE. The iodides of ethyl and methyl act upon morphine, producing hydriodates of bases in which 1 at. of the hydrogen of morphine is replaced by ethyl or methyl.

Hydriodate of Methyl-morphine, $C^{17}H^{18}(CH^{3})NO^{3}.HI.H^{2}O$, is very soluble in hot water, and is deposited on cooling in colourless rectangular needles, containing 4·04 per cent. water (= 1 at.). The solution treated with oxide of silver yields a brown amorphous mass, which is quickly attacked by iodide of methyl.

Hydriodate of Ethyl-morphine, $C^{17}H^{18}(C^{2}H^{5})NO^{3}.HI.H^{2}O$, produced by heating morphine with iodide of ethyl and a small quantity of absolute alcohol, in a sealed tube, is very soluble in boiling water, and crystallises on cooling in slender needles, containing 1·98 per cent. water. It is sparingly soluble in absolute alcohol, more soluble in ordinary spirit, permanent in the air. The aqueous solution is not precipitated by potash or ammonia. Hence this salt is probably analogous to iodide of tetrethyl-ammonium, and the group $C^{17}H^{19}O^{3}$ in morphine appears to be equivalent to 3 at. hydrogen.

The hydriodate is decomposed by oxide of silver, yielding a very caustic liquid which when evaporated leaves a dark brown amorphous mass. (H. How, Chem. Soc. Qu. J. vi. 125.)

MORPHIUM. Syn. with MORPHINE.

MORPHOLITES. Earthy concretions found in Sweden, consisting of marl with between 47 and 49 per cent. carbonate of calcium; they have a slaty structure with laminæ of unequal thickness and dissimilar colours. (See IMATRA STONES, p. 245.)

MORTAR. See *Ure's Dictionary of Arts, Manufactures, and Mines*, iii. 199.

MORVENITE. A brilliant variety of baryta-harmotome found at Strontian in Argyleshire (p. 13).

MOSAIC GOLD. *Or molu.* An alloy of copper and zinc in equal parts. (See COPPER, ALLOYS OF, ii. 49.)

MOSANDRITE. A silico-titanate of cerium, calcium, &c., found in radiate masses and imperfectly developed (monoclinic?) prisms, imbedded, together with leucophane, titaniferous iron, fluor-spar, &c., in the syenite forming the islet of Lammarskjäret, at the entrance of the Langesundfjord, near Brevig in Norway. It has a dark red-brown colour, vitreous to fatty lustre, and is usually more or less weathered. Hardness = 4. Specific gravity = 2·93 to 2·98. Contains 29·93 per cent. silica, 9·90 titanic anhydride, 26·56 oxides of cerium, lanthanum, and didymium, 1·83 ferric oxide, 0·75 magnesia, 19·07 lime, 0·52 potash, 2·87 soda, and 8·90 water (= 100·33). (Erdmann, Berz. Jahresb. xxi. 178.)

MOSS AGATE. See AGATE (i. 62).

MOTHER-LIQUOR or *Mother-water*. The portion of a mixed solution which remains after the less soluble salts or other bodies have crystallised out.

MOTHER-OF-PEARL. The hard silvery brilliant internal layer of several kinds of shells especially oyster shells, often exhibiting brilliant iridescence arising from the striated structure of its surface (see LIGHT, p. 608). It contains about 66 per cent. carbonate of calcium, 2·5 organic matter, and 31·5 water.

MOUNTAIN CORK or **MOUNTAIN LEATHER.** A variety of asbestos in which the fibres are so interlaced that the fibrous structure is not apparent.

MOUNTAIN BLUE. Syn. with AZURITE. (See CARBONATES, i. 783.)

MOUNTAIN GREEN. Syn. with MALACHITE. (See CARBONATES, i. 783.)

MOUNTAIN SOAP. See STEATITE.

MUCAMIDE. $C^6H^{12}N^2O^6 = \left.\begin{matrix}H^4\\(C^6H^4O^2)^{vi}\\H^4\end{matrix}\right\}\begin{matrix}O^4\\N^2\end{matrix}$ (Malaguti, Compt. rend. xxii. 854.)—Produced by the action of ammonia on mucic ether. It is white, very slightly soluble in boiling water, and separates on cooling in microscopic crystals having the form of an octahedron with rhombic base, truncated on both summits, and looking like bevelled plates. It is tasteless and insoluble both in alcohol and in ether. Specific gravity 1·589 at 13·5°. Heated with water to 136°–140°, it is converted into mucate of ammonium:

$$C^6H^{12}N^2O^6 + 2H^2O = C^6H^8(NH^4)^2O^8.$$

A boiling solution of mucamide mixed with ammoniacal acetate of lead forms a precipitate of ammoniacal mucate of lead or *mucate of lead and plumbammonium*, $C^6H^6Pb(NH^3Pb)O^8.3H^2O$. A boiling saturated solution of mucamide forms with ammoniacal nitrate of silver a specular deposit of metallic silver.

Mucamide turns brown when heated a few degrees above 200°, and yields by dry distillation, water, dipyromucamide, a small quantity of pyromucic acid, carbonic anhydride, and carbonate of ammonium; the residue contains carbon and paracyanogen.

MUCIC ACID. $C^6H^{10}O^8 = \left.\begin{matrix}H^4\\(C^6H^4O^2)^{vi}\\H^2\end{matrix}\right\}O^6$.—This acid, isomeric with saccharic acid, was discovered by Scheele in 1780, and has been examined chiefly by Laugier (Ann. Chim. xli. 79); Berzelius (*ibid.* xcii. 141; xciv. 5; xcv. 31); Malaguti (Ann. Ch. Phys. [2] lx. 195; lxiii. 86); Liebig and Pelouze (Ann. Ch. Pharm. xix. 258); Liebig (*ibid.* xxvi. 16) Hagen (Pogg. Ann. lxxi. 531); Johnson (Ann. Ch. Pharm. xciv. 225); and Schwanert (*ibid.* cxvi. 227); see also Gm. xi. 502; Gerh. ii. 143. It is dibasic, and was formerly represented by the diatomic formula $\left.\begin{matrix}(C^6H^8O^6)''\\H^2\end{matrix}\right\}O^2$, but from its relation to the sugars, it is now regarded as derived from the hexatomic alcohol $C^6H^{14}O^6$, by the substitution of 2 at. O for 4 at. H, being accordingly represented by the formula $\left.\begin{matrix}H^4\\(C^6H^4O^2)^{vi}\end{matrix}\right\}O^6$, the number of its basic hydrogen-atoms being, as in other similar cases, equal to the number of oxygen-atoms which have entered into it by substitution. (Kekulé, *Lehrbuch*, ii. 237.)

Mucic acid is formed by the oxidation of milk-sugar, lactose or galactose (p. 1023), melitose, dulcite, and various kinds of gum (viz. gum-arabic, tragacanth, &c.). It is prepared by heating milk-sugar with moderately dilute nitric acid. According to Guckelberger (Ann. Ch. Pharm. lxiv. 348), the best proportions are 1 pt. milk-sugar to 2 pts. nitric acid of specific gravity 1·42, the vessel being warmed till the reaction begins, then cooled, and afterwards gently warmed towards the end of the process. The product thus obtained, amounts to 60—65 per cent. of the milk-sugar employed. According to Pasteur, lactose treated with nitric acid yields twice as much mucic acid as milk-sugar. Gum-arabic may also be used for the preparation of mucic acid, 1 pt. of it being heated with 4 pts. nitric acid of specific gravity 1·35; but the acid thus obtained contains calcium-salts.

Crude mucic acid is purified by recrystallisation from boiling water, or better, especially if it has been prepared from gum, by dissolving it in ammonia, repeatedly crystallising the ammonium-salt from boiling water, and finally precipitating the mucic acid from the solution by nitric acid at the boiling heat.

Mucic acid crystallises in colourless tables with square base. It is sparingly soluble in cold *water*, soluble in 6 pts. of boiling water, and insoluble in *alcohol*. *Sulphuric acid* dissolves it with crimson colour.

Mucic acid boiled for some time with water undergoes an isomeric transformation, and is converted into an acid (paramucic acid) more soluble and more energetic than mucic acid: its salts are also more soluble than the mucates, but their solutions in boiling water deposit mucates on cooling.

Mucic acid heated *per se* first melts, and then decomposes, yielding, among other products, pyromucic acid and carbonic anhydride:

$$C^6H^{10}O^8 = C^5H^4O^3 + CO^2 + 3H^2O.$$

When oxidised by boiling with *nitric acid*, it yields racemic and oxalic acids (Carlet). Distilled with *sulphuric acid* and *peroxide of manganese*, it gives off formic acid. By heating with caustic *potash*, it is converted into a mixture of acetate and oxalate:

$$C^6H^{10}O^8 = 2C^2H^4O^2 + C^2H^2O^4.$$

Mucic acid is converted by *pentachloride of phosphorus* into a peculiar dibasic chlorinated acid, $C^6H^4Cl^2O^4$, which has not been thoroughly investigated, but evidently stands to mucic acid in the same relation as chloromaleic acid, $C^4H^3ClO^4$, to tartaric acid, $C^4H^6O^6$ (Liès-Bodart, Ann. Ch. Pharm. c. 325). Mucic acid heated with *hydriodic acid* is converted into an acid having the composition of adipic acid, $C^{10}H^{\cdot 8}O^4$. (Crum Brown, Ann. Ch. Pharm. cxxv. 19.)

Mucates. Mucic acid is dibasic. Its salts are for the most part neutral, of the form $C^6H^8M^2O^8$; but a few acid mucates of the alkali-metals are also known. The alkali-metal mucates are very soluble in water; the rest are mostly insoluble. The soluble mucates are decomposed by acids, with deposition of mucic acid. The mucates when heated give off the odour of caramel.

Mucates of Ammonium.—The *neutral salt*, $C^6H^8(NH^4)^2O^8$, is obtained by supersaturating the hot solution of the acid with ammonia, and repeatedly crystallising the salt which forms on cooling. The crystals are colourless flat four-sided prisms, which become soft and yellow at 220°, and between 220° and 240° are resolved into water, carbonic anhydride, carbonate of ammonium, pyromucic acid, and dipyromucamide, while small quantities of charcoal and parayanogen remain behind:

$$\underset{\text{Mucate of ammonium.}}{C^6H^8(NH^4)^2O^8} = \underset{\text{Pyromucic acid.}}{C^5H^4O^3} + \underset{\text{Carbonate of ammonium.}}{CO^3(NH^4)^2} + 2H^2O$$

$$\text{and } C^6H^8(NH^4)^2O^8 = \underset{\text{Dipyromucamide.}}{C^5H^6N^2O} + CO^2 + 5H^2O.$$

Possibly the pyromucic acid, formed as in the manner represented by the first equation, is converted into dipyromucamide by the action of the carbonate of ammonium formed at the same time.

Mucate of ammonium dissolves sparingly in cold, more freely in hot water: according to Malaguti, it is more soluble than the corresponding paramucate.

Acid mucate of ammonium, $C^6H^9(NH^4)O^8.H^2O$, prepared by neutralising 1 pt. of mucic acid with ammonia, and then adding an equal portion of the acid, crystallises in colourless needles or thin prisms which, after drying over oil of vitriol, give off 7·32 per cent. water (= 1 at.) at 100°. It is more soluble in water than the neutral salt, and when distilled yields the same products, together with a small quantity of a yellow oil, which is soluble in water, appears to boil below 100°, and quickly turns brown when exposed to the air.

The mucates of *barium*, *strontium*, and *calcium* are precipitated on adding mucate of ammonium to the chlorides. The *barium-salt* dried at 100° is $2C^6H^8Ba^2O^8.3H^2O$; the *calcium-salt* dried at 100°, has a similar composition.

Cupric mucate, $C^6H^8Ccu''O^8.H^2O$ (at 100°), is a bluish-white precipitate.

Ferrous mucate, $C^6H^8Ffe''O^8.2H^2O$ (at 100°), is a yellow powder precipitated by alkaline mucates from ferrous sulphate. It is permanent at ordinary temperatures, but takes fire between 150° and 160°.

Mucates of Lead.—A *hexbasic*(?) *salt*, is obtained by precipitating basic acetate of lead with mucate of ammonium. The *neutral salt*, $C^6H^8Ppb''O^8.H^2O$, is obtained by precipitating nitrate, chloride, or neutral acetate of lead, with mucic acid or mucate of ammonium. It gives off its water at 130°.

Mucates of Potassium.—The *neutral salt* forms white granular crystals, containing $2C^6H^8K^2O^8.H^2O$, which remain unaltered at 100°, but turn yellow and give off 1 at. water at 150°. The salt dissolves in 8 pts. of hot water, and separates almost completely on cooling; it is insoluble in alcohol. The *acid salt*, prepared like the acid ammonium-salt, forms transparent crystals, which when dried in the air or at 100° contain $C^6H^9KO^8.H^2O$.

Mucate of Silver, $C^6H^8Ag^2O^8$, is obtained by precipitating nitrate of silver with mucic acid or a soluble mucate. It does not give off anything at 100°.

Mucates of Sodium.—The *neutral salt* forms large transparent crystals containing $2C^6H^8Na^2O^8.9H^2O$ which give off 8 at. water at 100°, and obstinately retain the last atom. The solution, if rapidly boiled down, deposits a white powder, containing $2C^6H^8Na^2O^8.H^2O$.—The *acid sodium-salt*, colourless shining prisms, containing $2C^6H^9NaO^8,7H^2O$: they give off their water at 100°.

MUCIC ETHERS. *Amyl-mucic acid*, $C^6H^9(C^5H^{11})O^8$, is produced by the action of sulphuric acid on a mixture of amylic alcohol and mucic acid. It is crystallisable, dissolves in boiling water and in alcohol.

Mucates of Ethyl. The *neutral* compound, $C^{10}H^{18}O^8 = C^6H^8(C^2H^5)^2O^8$, commonly called *mucic ether*, is prepared by gently heating 1 pt. of mucic acid with 4 pts. of sulphuric acid till it turns black, then leaving it to cool, and adding 4 pts. of alcohol of specific gravity 0·814. The mixture left to itself for 24 hours solidifies in a mass, which must be shaken up with alcohol, thrown on a filter, washed with alcohol, and purified by repeated crystallisation from boiling alcohol.

Mucate of ethyl crystallises in transparent four-sided prisms, terminated by a single perpendicular face. It is insipid at first, but leaves a bitter aftertaste. It melts at 150°, and solidifies in a crystalline mass at 135°. At a higher temperature it is resolved into alcohol, water, carbonic anhydride, acetic acid, carburetted hydrogen, pyromucic acid, and charcoal. It is insoluble in ether, very soluble in boiling alcohol, very sparingly in cold alcohol; very soluble also in boiling water, which deposits it in well-defined crystals on cooling. The alkaline hydrates decompose it like other ethers: ammonia converts it into mucamide.

Ethylmucic acid or *Mucovinic acid*, $C^8H^{14}O^8 = C^6H^9(C^2H^5)O^8$. In the preparation of neutral ethylic mucate, it sometimes happens that an aqueous solution of that compound not yet pure, gives off all at once a very decided alcoholic odour, and yields by evaporation a substance totally different in appearance from the neutral ether. It is purified by treatment with alcohol, which removes the neutral ether, and the residue is crystallised two or three times from water. The product is pure when its solution is no longer rendered turbid by ammonia.

Ethylmucic acid is white, of asbestos-like aspect, the form of its crystals being that of a right prism with rhombic base. It is moderately soluble in water, very slightly in alcohol. It has a pure acid taste, and melts at 190°, with decomposition. The melted mass assumes a vitreous aspect on cooling, but after a considerable time it softens and again becomes opaque.

Ethylmucate of ammonium, $C^8H^{13}(NH^4)O^8$, is very soluble, tasteless, and has a slight acid reaction. Its solution precipitates the salts of *lead*, *silver*, *copper*, *barium*, and *strontium*, very slightly those of *calcium*, and forms no precipitate with salts of *zinc*, *magnesium*, &c. All the precipitates are soluble in acetic acid.

When a solution of ethylmucic acid is boiled with oxide of silver, carbonic anhydride is evolved, a portion of the oxide is reduced, and a silver-compound is formed, which explodes when slightly heated.

Mucate of Methyl, $C^8H^{14}O^8 = C^6H^8(CH^3)^2O^8$, is prepared like mucate of ethyl, and crystallises from water or alcohol in laminæ, or in flattened six-sided prisms, colourless, non-volatile, and tasteless. It is very soluble in boiling water, very little in boiling alcohol. It decomposes at 163° without melting, and then changes to a black liquid, which swells up, and gives off gases containing carbon.

MUCEDINEÆ. From experiments on the growth of these fungi (*Ascophora nigrans*), Ranlin (Compt. rend. lvii. 771) concludes that they require for their normal development the elements of phosphate and sulphate of ammonium and of the carbonates of potassium, magnesium and manganese, but that these elements are not all of equal value to them. If 20 grms. of the plant are produced in a given time in a liquid containing all the substances above mentioned, then in the same time there will be formed, in the absence of manganese, 5 grms.; of sulphur, 2 grms.; of potassium and magnesium, only 1 grm.; and in the absence of phosphorus, only half a gramme of the plant. Experiments in which these fungi were developed in a confined volume of air, showed that the nitrogen of the air was not essential to their growth. Similar results, so far as regards the mineral constituents, have been obtained with plants of higher orders, by G. Ville (Compt. rend. lvii. 270).

MUCILAGE. The gum of seeds, roots, &c. (See Gum, ii. 955.)

MUCIN. The name of one of the constituents of gluten (ii. 873); also of the chief constituent of animal mucus.

MUCUS. The normal secretion of mucous membranes. It is found in the respiratory, genito-urinary, digestive, &c. passages of animal bodies, mingled in certain situations with specific fluids furnished by special glands. It is very doubtful, however, whether the secretion ought to be considered as the same in all cases, whether in fact there is a one thing, mucus, modified by the addition of other matters from time to time, and not a different secretion altogether for each membrane or organ. When obtained in a state of approximate purity, mucus appears as an alkaline fluid of a very peculiarly glairy, ropy nature. Under the microscope are seen, besides fatty and other granules, epithelial scales, varying in form and kind according to the nature of the membrane from which the mucus is obtained, and the so-called mucus-corpuscles, which differ in no essential respect from pus-corpuscles. These morphological elements vary exceedingly in number in different specimens, but are rarely, if ever, wholly absent.

Among the chemical constituents, the most important is mucin, a colloïd substance, existing in the liquid in an undissolved condition. To its presence is due the peculiar ropiness of the secretion.

Mucin is insoluble in water, and can be separated from it by filtration, though Scherer found on one occasion a mucus which was soluble in water and readily passed through the filter. Heat produces no coagulation; on the contrary, a real solution seems to be thereby effected. It may be precipitated by alcohol as a flocculent stringy mass, which on the subsequent addition of water, will swell up into its former colloïd state. Dilute acetic acid and mineral acids precipitate it; concentrated acids dissolve it readily; alkalis, especially when dilute, also dissolve it. From its solution in weak acids it may be precipitated by alkalis added with caution. Ferrocyanide of potassium produces no precipitate either in alkaline or acid solutions, except when a solution in strong acetic acid has been boiled. Tannic acid and basic acetate of lead throw it down from a faintly alkaline solution; the neutral acetate and mercuric chloride produce only a slight turbidity. Concentrated hot nitric acid colours it yellow. The addition of a large quantity of water generally coagulates it, probably owing to some of the solvent alkalis being thereby withdrawn. The difficulty of obtaining it pure detracts from the value of any elementary analysis. According to Scherer, 100 parts of it contain carbon 52·4, hydrogen 7·0, nitrogen 12·8, oxygen 27·8. It contains no sulphur, but gives 4 per cent. ash, consisting chiefly of phosphate of calcium and alkaline carbonates. Mucin is found not only in ordinary mucus, but also in synovia, in the contents of various cysts, in the pathological product known as "colloïd tissue" and in the unformed connective tissue of the umbilical cord and embryo.

Besides mucin, mucus contains a very small quantity of fat, various extractive matters, and salts. Among the latter are sulphates and phosphates of the alkali-metals, with earthy phosphates and especially alkaline chlorides. According to Berzelius, 100 parts of nasal mucus contain 93·37 water, 5·33 mucin and ·56 alkaline chloride. Albumin is very often found in mucus, but may be regarded as an abnormal constituent. In certain pathological states, various forms of albumin are poured out in abundance on the surface of mucous membranes, as transudations. The secretion is also said at times to change from mucous into muco-purulent or purulent (see Pus).

It has been thought that mucus was generated by the breaking-up of the epithelium of the mucous membranes. The want of relationship, however, between the number of such epithelium scales and the amount of mucin in any given quantity of mucus, and the presence of mucin in embryonal connective tissue, negative such an idea. Probably mucin is not secreted by the mucous membrane as such, but is developed on the free surfaces out of some unknown antecedents, perhaps in some such way as fibrin is formed out of its peculiar antecedents.

The great use of mucus seems to be to lubricate the passages where it is found. A ferment-action has been largely attributed to it. The mucus present in urine is said to be a chief cause of the change which urea speedily undergoes into carbonate of ammonium in exposed urine. The weak power of converting starch into sugar possessed by many mucus-bearing fluids, not containing saliva, has been supposed to be due to the mucus. This however is doubtful. The catalytic action of urine on starch certainly does not reside in its mucus (Cohnheim). In the mucus of the respiratory passages (sputa) during certain pathological states (bronchitis), the alkaline chlorides are much increased. M. F.

MUDARIN. An extractive matter obtained from mudar-root, the root of *Asclepia gigantea*, L. (A. Duncan. Fontenelle, Ann. Ch. Pharm. xvii. 210.)

MUDESIC ACID. A product of the oxidation of mudesous acid.

MUDESOUS ACID. $C^{12}H^{10}O^{8}$ (?)—An organic acid, which, in combination with alumina, forms the mineral called *Pigotite*, found coating the walls of certain granite caverns in Cornwall. Pigotite is brown; yields a yellowish powder; is insoluble in water and alcohol; gives off 27 per cent. water in drying; and decomposes at higher temperatures, giving off empyreumatic products, and leaving alumina mixed with charcoal. The acid separated from the alumina is dark-brown, permanent in the air, soluble in water, forms a deliquescent ammonium-salt, and gives brown precipitates with metallic salts. Nitric acid converts it into mudesic acid, a brownish-yellow substance, said to contain 2 at. oxygen more. Mudesous acid is supposed to have been formed from the remains of plants, its aqueous solution dissolving the alumina of the decomposed granite as it percolated through the cavities. (Johnston, Handw. d. Chem. v. 406; vi. 502.)

A substance from Wicklow in Ireland, probably identical with Pigotite, has been examined by Apjohn (Jahresb. 1852, p, 903).

MULHOUSE BLUE. A blue dye, obtained by prolonged boiling of an alkaline solution of shellac with aniline-red. (Schaffer and Gros-Renaud, Bull. Soc. Industr. de Mulhouse, xxxi. 238; Rép. Chim. app. iii. 273.)

MÜLLER'S GLASS, or *Hyalite*. A variety of OPAL (*q. v.*).

MULLERITE. Syn. with SYLVANITE.

MULLICITE. Syn. with VIVIANITE.

MULTIPLIER, or *Galvanometer* (see ELECTRICITY, ii. 443).

MUNJEET. *Rubia Munjista.*—This plant, also called *East Indian madder*, is extensively cultivated in India, its root being used as a dyestuff for producing colours similar to those obtained from ordinary madder. The colouring matters contained in it are, however, by no means identical with those of common madder; in fact, Stenhouse has shown that it contains no alizarin, but that its colouring matter is a mixture of purpurin and an orange-dye, called munjistin (see the next article). The colours which it produces are brighter than those of ordinary madder, but not so durable.

The tinctorial power of munjeet was first examined by Runge in 1835, who reported that it contained about twice as much available colouring matter as ordinary madder; but subsequent experiments, both by German and by English dyers, have shown that this result was incorrect, and that the colouring power of munjeet is actually much less than that of ordinary madder.

The actual amount of colouring matter in munjeet is indeed very nearly the same as in the best madder. Stenhouse finds that the garancin from munjeet has about half the tinctorial power of that made from the best madder, viz. Naples roots; these, however, yield only about 30 to 33 per cent. of garancin, whereas munjeet, according to the experiments of Mr. Higgin of Manchester, yields from 52 to 55 per cent.

The inferiority of munjeet as a dyestuff results from its containing only the comparatively feeble colouring matters purpurin and munjistin, only a small part of the latter being available, while its presence in large quantity appears to be positively injurious; so much so, indeed, that munjeet-garancin, freed by boiling water from the greater part of the munjistin which it contains, yields much richer shades with alumina-mordants than before. (Stenhouse, Proc. Roy. Soc. xiii. 148.)

MUNJISTIN. $C^8H^6O^3$. (Stenhouse, Proc. Roy. Soc. xii. 633; xiii. 86, 145.)—An orange colouring matter contained, together with purpurin, in munjeet or East Indian madder. It is nearly related in composition to purpurin, $C^9H^6O^3$, and alizarin, $C^{10}H^6O^3$, differing from the former by 1 at. and from the latter by 2 at. carbon. It exists in munjeet in considerable quantity, and may be extracted by the following process:—

Each pound of munjeet in fine powder is boiled for four or five hours with 2 pounds of sulphate of aluminium and about 16 pounds of water, the operation being repeated two or three times; the red liquor thus obtained is strained through cloth filters while still very hot; and the clear filtrate is saturated with hydrochloric acid, whereby a bright-red precipitate is soon produced, which goes on increasing in quantity for about twelve hours if the liquid is left at rest. This precipitate is collected on cloth filters, and washed with cold water till the greater part of the acid is removed; then dried, pulverised, and digested in a percolator with boiling sulphide of carbon, which dissolves the crystallisable colouring principles of the munjeet, and leaves a considerable quantity of dark-coloured resinous matter. The excess of sulphide of carbon having been removed by distillation, the bright-red extract, consisting chiefly of a mixture of munjistin and purpurin, is repeatedly treated with moderate quantities of boiling water and filtered, the clear yellow filtrate consisting of a solution of munjistin, while nearly all the purpurin remains on the filter. The solution acidulated with hydrochloric or sulphuric acid deposits the munjistin in large yellow flocks, which are slightly washed on a filter with cold water, then dried by pressure, and dissolved in boiling spirits of wine, slightly acidulated with hydrochloric acid, to remove any adhering alumina. As the munjistin does not subside from cold alcoholic solutions, even when they are largely diluted with water, about three-fourths of the spirit must be distilled off, after which the munjistin is deposited in large yellow scales. By two or three crystallisations from spirit, in this manner, it may be rendered perfectly pure.

Munjistin may also be extracted directly from munjeet by boiling with water, acidulating the dark brownish-red filtrate with hydrochloric acid, and treating the precipitate as above; but the process above described yields a better product. The colouring matter of munjeet may also be extracted by boiling solutions of alum; but sulphate of aluminium is better adapted for the purpose, as the alum, by its tendency to crystallise, greatly impedes the filtration of the liquids. E. Kepp's process with sulphurous acid (p. 749), is not applicable to munjeet.

Properties.—Munjistin crystallises from alcohol in golden-yellow plates of great brilliancy. It is but moderately soluble in cold, but dissolves pretty readily in boiling *water*, forming a bright-yellow solution, from which it is deposited in flocks on cooling. It dissolves to some extent in cold but more readily in boiling *alcohol*, and is not precipitated therefrom by water. It dissolves, with bright-red colour, in aqueous *carbonate of sodium;* with *ammonia*, it forms a red solution, having a slight tinge of brown; with *caustic soda*, it produces a rich crimson colour.

Munjistin, in some of its properties, bears considerable resemblance to the rubiacin of Schunck (madder-orange of Runge, p. 742); but according to Stokes (Proc. Roy. Soc. xii. 637), the two substances are perfectly distinguished by the colours of their solutions in carbonate of sodium, when a small quantity only of each is used, the solution of munjistin being red inclining to pinkish-orange, while that of rubiacin is claret-red; also by the absorption-bands which are seen on examining the spectra of these solutions (see LIGHT, p. 638); both present a single minimum in the spectrum; but while that of rubiacin extends only from about D to F, that of munjistin extends from a good way beyond D to some way beyond F. A further distinction is afforded by the characters of the fluorescent light of the ethereal solutions of these substances, that of rubiacin being orange-yellow, while that of munjistin is yellow inclining to green.

Munjistin sublimes more readily than either purpurin or alizarin, forming golden-yellow scales consisting of the unaltered substance. Neither sublimed munjistin, nor that obtained by crystallisation from alcohol and drying in a vacuum, loses any weight at 100°. When carefully heated in a tube it melts, and crystallises again on cooling. When strongly heated on platinum-foil, it readily takes fire, and burns away without residue.

Munjistin dissolves readily in cold *sulphuric acid*, forming a bright-orange solution which may be heated nearly to boiling without blackening or evolution of sulphurous acid, and on dilution with water, deposits the munjistin in yellow flocks apparently unaltered. By digestion with moderately strong *nitric acid*, it is converted (like alizarin and purpurin) into phthalic acid, $C^8H^6O^4$, together with a small quantity of oxalic acid.

Bromine-water added to a strong aqueous solution of munjistin throws down a pale-coloured flocculent precipitate, which when dissolved in hot alcohol, yields tufts of crystals, evidently a substitution-product.

Baryta-water forms a yellow precipitate with solutions of munjistin. *Acetate of copper* forms a brown precipitate very slightly soluble in acetic acid. *Acetate of lead* added either to the aqueous or to the alcoholic solution, throws down a bright-crimson precipitate, which when washed with alcohol and dried in a vacuum, contains, on the average, 34·8 per cent. carbon, 1·9 hydrogen, and 48·5 lead-oxide: agreeing nearly with the formula $Pb^2O.10C^8H^5PbO^3$, analogous to that of the lead-compound of purpurin, $Pb^2O.10C^9H^5PbO^3$, described by Wolff and Strecker (see PURPURIN).

Both the aqueous and alcoholic solutions of munjistin, when boiled with *alumina*, form a beautiful lake of a bright orange-colour, almost the whole of the munjistin being withdrawn from solution. This lake is soluble in a large excess of caustic soda, producing a fine crimson solution. Munjistin dyes cloth mordanted with alumina a bright orange; with iron mordant it yields a brownish-purple colour, and with Turkey-red mordant a pleasing deep orange. These colours are moderately permanent, and bear the application of bran and soap tolerably well.

When an ammoniacal solution of munjistin is exposed to the air, in a warm place, the munjistin is gradually but completely decomposed, the greater part being changed into a brown humus-like substance insoluble in ammonia; while the remainder forms a non-crystalline colouring substance, analogous to purpureïn (the product formed in like manner from purpurin, *q. v.*), and capable of dyeing *unmordanted* cloth of a brownish-orange colour.

MUNTZ'S METAL. An alloy of copper and zinc used for sheathing ships, and for other purposes (see COPPER, ALLOYS OF, ii. 49).

MURCHISONITE. A yellowish-grey or flesh-red variety of felspar from Heavitree, near Exeter.

MUREXAN. *Dialurimide* (Laurent).—Discovered by Prout in 1818 (Ann. Ch. Phys. xi. 48), who called it *Purpuric acid:* further examined by Kodweiss (Pogg. Ann. xix. 12), and by Liebig and Wöhler (Ann. Ch. Pharm. xxvi. 327). It is formed by the decomposition of murexide by the stronger acids, sulphuretted hydrogen, or potash. It is obtained by adding sulphuric or hydrochloric acid to a boiling

solution of murexide in water or potash: the crystalline
dissolving it in cold sulphuric acid, and precipitating by wa
in potash, and precipitating it by an acid. It is thus obta
powder, lustrous like uramil, infusible, tasteless, and does
turns red in air containing ammonia. It is almost insol
quiring more than 10,000 pts.: insoluble in alcohol, ether,
chloric, or phosphoric acid, or in aqueous, acetic, tartaric, or c
in cold strong *sulphuric* acid, and reprecipitated by water;
without neutralising them, forming solutions which are col
cluded.

Murexan is decomposed by *dry distillation*, yielding cyanic
It is dissolved and decomposed by *chlorine-water*, withou
When heated with strong *nitric acid* it is dissolved with
nitrous and carbonic anhydrides, and yielding on evaporatio
murexan (Kodweiss). When heated with *sulphuric acid*, i
dride and a little nitrogen, and forms a brown solution, conta
precipitable by water. Its colourless solution in *ammonia*
posed to the air, and on evaporation yields crystals of murexi

$$\underset{\text{Murexan.}}{C^8H^7N^5O^6} + O + NH^3 = \underset{\text{Murexide.}}{C^8H^8N^6O^6}$$

The purple solution is decolorised by exposure to oxygen-gas,
being formed.

Under certain circumstances murexan appears to combine w
in warm dilute *nitric acid* without effervescence, and yield
rhombohedra, which appear to be nitrate of murexan. When
containing a little nitric acid, or when heated with strong nitri
by evaporation, which, according to Kodweiss, are oxalate of

The composition of murexan is very variously stated. The
Wöhler, and of Kodweiss, yield very conflicting results:
ably with the formula $C^8H^4N^2O^{2\frac{1}{2}}$, which is accordingly adopted b
Gerhardt (*Chim. org.* i. 1517) considers murexan as iden
$C^4H^8N^2O^3$: a view which is advocated by Beilstein (Ann.
according to whose analyses murexan contains 29·54 per cent.
tolerably with 29·38, the calculated percentage in $C^4H^8N^2$
formula $C^8H^7N^5O^6$, which gives percentages intermediate betw
leads to the simplest equations. Laurent (Compt. rend. xx
formula, and regards the compound as dialurimide—N.C^8H^6N

	calc. L. and W.		L. and W.	Kodweiss.	
C^3	36	33·33	33·32	36·58	C
H^4	4	3·70	3·72	2·22	H
N^2	28	25·93	25·72	28·45	N
$O^{2\frac{1}{2}}$	40	37·04	37·24	32·75	O
$C^3H^4N^2O^{2\frac{1}{2}}$	108	100·00	100·00	100·00	C^8H^7N

MUREXIDE. See PURPURATES.

MUREXOIN. A product formed by the joint action
amalic acid, and crystallising from warm water or alcohol
four-sided prisms, two faces of which reflect light with gold-ye
tion of this compound resembles that of murexide, excepting
instead of being turned blue by potash, also by evaporation
it gives by analysis numbers agreeing approximately with th
(Rochleder, J. p. Chem. li. 398; Jahresb. 1850, p. 434.)

MURIACITE. Syn. with ANHYDRITE (i. 295).

MURIATIC ACID. The old name of chlorhydric or h

MUROMONTITE. A variety of orthite (*q. v.*) from Ba
Saxony.

MUSA. The ripe fruit of the Banana (*Musa paradisiaca*)
tains, according to Corenwinder (Compt. rend. lvii. 781), 7
albumin, 0·2 cellulose, 0·63 fats, 19·66 cane-sugar and inverte
organic acids, pectose, and traces of starch), 0·06 phosphor
lime, alkalis, iron, chlorine, &c. The ash of the husk of the
contain 47·98 carbonate of potassium, 6·58 carbonate of so

potassium, 5·66 alkaline phosphates (with a little sulphate), 7·50 charcoal, 7·10 lime, silica, earthy phosphates, &c. (= 100).

In the milky juice of the flower-stem of the same plant, Comnille (J. Pharm. [3], xliii. 269) found 25·27 per cent. potash, 9·52 soda, 15·85 lime, 5·00 magnesia, 0·87 alumina, with a trace of ferric oxide, 6·30 chlorine, 0·96 sulphuric anhydride, 0·87 phosphoric anhydride, 0·81 silica, and 34·17 carbonic anhydride (calculated from the bases).

MUSCLE. See MUSCULAR TISSUE.

MUSCOVITE. Potash-mica. (See MICA, p. 1010.)

MUSCULAR TISSUE. A. *Striated muscles,—Voluntary Muscles,—Muscles of animal life,—Muscles taking part in energetic movements.*—These consist of parallel primitive bundles of fibres bound together with fatty and connective tissue, the latter affording gelatin, not proper to muscular tissue itself. Each fibre may be considered as a tube consisting of—1. A sheath or *sarcolemma*, resembling, physically and chemically, elastic tissue;—2. *Nuclei*, whose exact chemical composition is unknown;—3. The *muscle-substance* or *fluid* (semifluid) contents of the sheath, marked with the transverse striæ;—4. *Granules*, &c., mostly fatty;—5. Terminations of nerves &c. (?)

The living fibre is contractile, and very extensible (slight but very perfect elasticity); its substance is transparent. When the nutrition of a muscle is arrested, contractility is lost, and the condition known as *rigor mortis* comes on. The fibre is then opaque, is shorter and thicker than during life, and has lost much of its extensibility. The peculiar rigidity thus brought about passes away as putrefactive decomposition sets in.

The rapidity with which rigor mortis appears in the muscles of an animal, after somatic death, depends upon a variety of circumstances. An apparently identical rigidity may be instantaneously brought about by plunging muscles in water or oil, at a temperature of 40° (for cold-blooded animals, 49°—50° for mammals, 53° for birds; Kühne, *Myolog. Untersuch.*), or by injecting into the blood-vessels various substances, such as chloroform (Küssmaul, Virchow Archiv. xiii. p. 289). Rigor mortis has been considered as a species of contraction,—"the last vital effort of the dying muscle," or the natural condition into which a muscle falls, when no longer sustained by life (Radcliffe). It seems more probable, however, as will be seen below, that it is due to a spontaneous coagulation of the muscle-substance.

The reaction of the living fibre, when freed as far as possible from blood, is neutral or amphichromatic. After death, with the onset of rigor mortis, it becomes acid, and continues so until changed by ammoniacal compounds generated in putrefaction. The acid is probably formed first in the interior of the fibre, for the natural surface of the muscle remains neutral the longest; and if it be due to any process of oxidation, the oxygen must be furnished by the muscle-substance itself, since the presence of external oxygen is wholly unnecessary. The reaction cannot be attributed to the acid phosphate of potassium, for the mark on litmus is permanent, which in that case it would not be. It is generally supposed to be due to lactic (sarcolactic) acid. When rigor is artificially produced by a temperature of 40° (frogs), the reaction at the same time becomes acid. When muscles, however, are plunged into water at 75°, they coagulate immediately, with a distinctly alkaline reaction, and at intermediate degrees are neutral, with a tendency to acidity or alkalinity. The alkaline reaction at 75° is not due to any destruction of a temporarily formed acid, or to any neutralisation of it by the alkali set free by the coagulation of the albumin; for muscles which have once become acid remain so, even when immersed for some time in boiling water. So also muscles coagulated by being plunged into alcohol remain neutral. There seems, therefore, to be no causal connection between rigor mortis and the post-mortem acid reaction. (Du Bois-Reymond, *Moleschott. Untersuch*, 1860, p. i.)

Though rigor mortis may be considered as a sign of death, the injection of blood through the vessels of a rigid limb will remove rigidity and restore contractility. (Stannius, Brown-Sequard). Kühne, however (*op. cit.*), denies that any such revival can take place when rigidity and acidity have fairly set in. The rigidity nevertheless may be removed by an injection of chloride of sodium, and Kühne makes (*Untersuch. über Protoplasma*) the interesting observation that the acid reaction disappears at the same time; and Preyer (Central-blatt. med. wissensch. 1864, p. 769), states that if a blood-injection follow the chloride of sodium injection, contractility may be restored.

The *muscle-substance*, whose fluidity is indicated by the wave-like phenomena of its contractions, by its movement towards the negative pole during the passage of an electric current (Kühne), and by the behaviour of living parasites lodged within the sarcolemma, was supposed by Brücke, and has been shown by Kühne (*op. cit.*), to contain a body whose spontaneous coagulation brings about the rigidity and opacity of the dead fibre. If a frog be opened, a 1 per cent. solution of chloride of sodium driven through the blood-vessels until all blood is removed, the muscles then rapidly chopped up and subjected to firm pressure, a liquid will be obtained, which in a short time sets into a firm coagulum, while the remaining fragments of muscle show a great lack of rigidity. In such an experiment, however, much of the muscle-substance will, through the treatment, be rendered rigid before the liquid can be expressed from it. In order to obtain an amount of coagulation sufficient to justify the idea that the rigidity is due to a coagulation of the muscle-substance itself, and not of any lymph or plasma bathing the fibres, muscles freed from blood by the injection of the (1 per cent.) solution of chloride of sodium are frozen, minutely divided, mixed with four times their volume of snow containing 1 per cent. of chloride of sodium, and the mass pulverised as far as possible. At − 3° the mixture will become sufficiently liquid to be filtered through linen; at 0° it may be rapidly passed through filtering paper. The filtrate then appears as a slightly opalescent fluid, which, exposed to ordinary temperature, will speedily set into a coagulum so firm, that the containing vessel may be turned over without any fear of spilling the contents. At a temperature of 40° coagulation takes place instantaneously. On standing the coagulum contracts, after the fashion of a blood-clot, but shows a great tendency to the production of flocks and flakes, and leaves the surrounding liquid highly opalescent. Adopting the phraseology used in speaking of blood, the fluid parts of muscle may be described as forming a muscle-plasma, which separates into the muscle-clot and muscle-serum.

The act of coagulation may fairly be supposed to be, like that of blood, the union into an insoluble compound of two soluble factors. **Kühne** found that one of the factors of blood-coagulation, viz. globulin, increased and hastened the coagulation of muscle-plasma. The cause or determining circumstance of the coagulation is unknown.

Myosin (the name given by **Kühne** to the muscle-clot) is, when thoroughly washed, completely neutral, forms when wet a white mass of little transparency, when dry a yellow horny substance. It gives the usual protein reactions, and contains sulphur. It is insoluble in water, alcohol, and ether, exceedingly soluble in very dilute acids, and alkalis, and in solutions of neutral salts of all degrees of concentration. In a 10 per cent. solution of chloride of sodium it is especially soluble, and may by this means be extracted from muscles already coagulated. (Hence in brine there is always to be found a considerable quantity of it.) If such a solution in chloride of sodium be added drop by drop to distilled water, the myosin is precipitated in flakes or lumps, sometimes as little vesicles. The precipitate so formed is unaltered myosin, and is readily redissolved in the chloride of sodium solution. The precipitate obtained, however, by the neutralisation of dilute acid or alkaline solutions of myosin is no longer myosin; it has changed in character, is no longer soluble in the chloride of sodium solution, and exhibits the reactions of syntonin.

In muscle-serum (that is, muscle-plasma minus muscle-clot or myosin) **Kühne** recognises at least three forms of albumin:—

1. An albumin whose coagulation depends in great part on the degree of acidity possessed by the serum. If abundance of acid be present, coagulation will occur at a temperature so low as 30°. In this body **Kühne** recognises the mixture of potassic albuminate and sodic phosphate described by **Rollett**.

2. An albumin coagulating at 45°.

3. A large quantity of albumin coagulating at 75°. There are also in untouched muscle other forms coagulating at 90°. The first form had been previously recognised by **Harless** (Henle u. Meissner's Bericht, 1859, p. 471), and was regarded by him as the chief cause of rigor mortis. And even though the formation of myosin, which is quite independent of the formation of acid, be considered as the chief part of rigor mortis, yet the subsequent coagulation caused or favoured by the presence of the acid will undoubtedly increase that condition.

Before the researches of **Kühne**, muscle was considered to consist of a small quantity of albumin and of a large quantity of syntonin. Myosin is not the same thing as syntonin. **Kühne** contends that syntonin does not exist as such in the untouched muscle, but is an artificial product due to the action of the dilute acid on myosin and other albuminoid bodies. He attributes the rapidity of the solution of the muscle-substance to the conjoined action of pepsin (the presence of which in muscles has been shown by **Brücke**), and affirms that a formation of syntonin always precedes that of the peptones in every digestion of albumin. v. **Wittich** (Königsberg. med. Jahrb. iii. 210) also adopts the same view (see SYNTONIN). Hence muscle-fibrin or syntonin prepared by Liebig's method would be regarded as consisting of myosin and the albumin coagulating at 30°; muscle-juice as a mixture of the other forms of albumin.

The *Heart* is singular in being an involuntary muscle, and yet being composed of striated fibres. It is remarkable for containing inosite, which is not found in other muscles. The alcoholic extract exhibits that excess over the watery extract which is characteristic of muscles actively exercised. Its reaction is the same as that of other striated muscles. (Du Bois-Reymond.)

B. *Non-striated, smooth muscles,—Involuntary muscles,—Muscles of organic life,—Muscles taking part in slow movements,—Contractile fibre-cells.*—These consist of long spindle-shaped cells, or riband-like fibres, marked with peculiar rod-like nuclei, and bound together with connective tissue, bloodvessels, nerves, &c. Greater difficulty is met with in the analysis of this variety, since the fibres are but seldom found in large isolated masses, and are much mixed up with other tissues. The "juice" is less in quantity and often mixed with other fluids. Lehmann found the reaction of the juice of the muscular coat of the pig's stomach distinctly acid, that of the middle coat of arteries feebly acid, that of *Tunica Dartos* neutral (*Lehrbuch*, iii. p. 62). Du Bois-Reymond however, found the muscles of the gizzard of fowls and pigeons always faintly alkaline after death, as also the muscular coat of intestines and arteries of oxen. Schultze too (Ann. Ch. Pharm. lxxi. p. 277) had previously observed the same reaction. Yet Siegmund (Verh. phys. med. Gesellsch. Wurzburg, iii. 50) discovered in the uterine muscles, acetic, formic, and lactic acids. From the smooth muscles a substance apparently identical with the syntonin of striated muscles may be obtained; and since the former exhibit rigor mortis, they also probably contain a form of albumin capable of coagulating spontaneously. Schultze (*op. cit.*) obtained from the smooth muscles of the middle coat of arteries a large quantity (7 to 21 per cent. of total dry matter) of a substance which he believed to be casein. Creatine is found in small quantities. The proportion of potash to soda is much less than in striated muscles—38 : 62 in the muscles of the stomach, 42 : 58 in the middle coat of the arteries. This would seem to imply a great mixture of blood-serum.

C. *Muscles of Invertebrata.*—These are in some classes striated (e. g. *Articulata*); in others, non-striated (e. g. *Mollusca*), and yet more closely allied with the striated than with the non-striated variety of vertebrata.

They probably agree in their main chemical feature with other muscles. Bernstein (Centralblatt für med. Wissensch. 1863, p. 437) found the muscles of the crab neutral or faintly alkaline when living, but becoming acid with the onset of rigor mortis. He also obtained a spontaneous coagulation of the expressed muscle-juice. In bivalve muscles he found the foot neutral, the adductors always acid. Both gave a spontaneously coagulating juice.

Valenciennes and Frémy (Ann. Ch. Phys. i. 129) found oleophosphoric acid to replace the acid phosphate of potassium in the muscles of the crab, and in molluscs they ascertained the absence of creatine and creatinine and the presence of taurine.

D. *Protoplasma,—Sarcode.*—The bodies of many of the lower animals consist in great part of a semifluid substance, capable of peculiar movements. A similar matter is also found in vegetable cells and in the cells of certain parts of animals (cornea, connective tissue). From the researches of Schultze (*Das Protoplasma*) and Kühne (*op. cit.*) it appears that this protoplasm is contractile, spontaneously coagulating, and exhibits other reactions which bespeak for it a close alliance with muscle-substance.

Metamorphosis of Muscular Tissue.—The chemical changes taking place in the living muscle, though most imperfectly known, may be generally described as those of oxidation. Living muscles consume oxygen and produce carbonic acid (Liebig, G. Müller's Archiv. 1850, p. 409; Matteucci, Compt. rend. 1856, i. 14; Valentin, Archiv. Physiol. Heilk. N.F. i. p. 285); the excretion of carbonic acid is continued when the muscle is placed in hydrogen-gas. Products of oxidation of nitrogenous material are always present in muscle—creatine, creatinine, inosic acid (proteic acid), hypoxanthine, taurine, leucine, &c.

On comparing the chemical composition of muscles at rest with that of muscles at work, it is found that by the act of contraction, the substances soluble in alcohol are increased and those soluble in water diminished (Helmholtz); the carbonic acid exhaled and the oxygen consumed are increased, the proportion of carbonic acid to oxygen being at the same time also increased (Matteucci, Valentin, *op. cit.;* Sczelkow, Zeitsch. nat. Med. xvii. p. 106); the substances given up to the blood are increased, (Cl. Bernard, Med. Times and Gaz. 1861, ii. p. 26); creatinine is increased partly at the expense of creatine. Heidenhain (*Mechanische Leistung, &c., bei der Muskelthätigkeit*) finds the amount of acid produced to be proportional to that of the actual energy liberated during the contraction (Sarokow, Virchow's Archiv. 28, p. 544). A muscle when tetanised becomes acid from a development of lactic acid (Du Bois-Reymond, *op. cit.*). It is uncertain whether this acid is a product newly formed or a permanent constituent temporarily increased in amount. Borszezow (Würburg. natur. Wissensch. Zeitsch. ii. p. 65) finds no lactic acid in living hearts; Folwarczny

(Henle u. Meissner, 1861, p. 295), however, finds it. With regard to creatine, Borszezow (*op. cit.*) believes that it is formed at the expense of creatinine, while Neubauer (Zeitsch. analyt. Chem. 1863, p. 22) regards creatinine as an artificial production and no natural constituent of muscle.

The position of the carbo-hydrates in muscle is a very uncertain one. In the muscles of the embryo, glycogen is found in abundance (Bernard, Journal de Physiolog. ii. p. 39; Rouget, *ibid.* p. 333); in the muscles of adults, occasionally. (McDonnell, Nat. Hist. Rev. iii. 538.)

Besides inosite, which exists in the muscles of the heart, Meissner (Henle u. Meissner, 1861, p. 295) has found in the muscles of the system, a fermentable sugar (not arising from food), which presents, as he thinks, some differences from hepatic sugar, and is probably due to muscular metamorphosis. Harley (Brit. For. Med. Chir. Review, 1857) and Chauveau (Gaz. Med. No. 23), however, find reason to believe in the destruction of sugar in the systemic capillaries (and therefore in part at least in the muscles).

Since exercise, *cæteris paribus*, increases rigor mortis, it might be inferred that one at least of the factors of myosin was developed during muscular metamorphosis. In the generally adopted views, the nitrogenous muscle-substance, the 'plastic' element, is supposed to supply by its conversion the force of muscular movements. Others (Traube) have maintained that the hydrocarbons and carbo-hydrates (of blood and muscle) are to be regarded as the main source of power. M. F.

MUSENA BARK. This bark, used in Abyssinia as an anthelmintic, contains, according to Thiel (J. Pharm. [3] xlii. 176), a sharp-tasting colloïdal substance called musenin, soluble in water and in alcohol, insoluble in ether.

MUSENITE. Cobalt-pyrites from Müsen, near Siegen, in Prussia (i. 1050).

MUSK. *Musc, Moschus.*—An odoriferous resinous substance contained in a bag near the navel of the male musk-deer, a small animal inhabiting Tonquin and Thibet. Musc occurs in commerce in brownish clots, often mixed with hair, sand, fat, and resins It has a bitter taste, a persistent odour, is very inflammable, and partially soluble in water and in alcohol. According to an analysis by Geiger and Reimann, it contains in 100 parts, 1·1 parts fat, 4·0 cholesterin, 5·0 bitter resin, 7·5 alcoholic extract (lactic acid-salts), 36·5 salts soluble in water (potash and ammonia, combined with a peculiar animal matter), 45·5 ammonia combined with lactic acid and water, and 0·4 sand. (Pelouze et Frémy, *Traité*, vi. 240. See also *Ure's Dict. of Arts, &c.*, iii. 211.)

MUSSEL-SHELLS. See Shells.

MUSSITE. Syn. with diopside or white augite (see Augite, i. 475).

MUSSONITE. Syn. with Parisite.

MUST. The juice of the grape, expressed for making wine, but not yet fermented (see Wine). The same term is also applied to the freshly-expressed juice of apple. and pears, previous to conversion into cider and perry by fermentation.

MUSTARD. The seeds of black and white mustard (*Sinapis nigra* and *S. alba*), when ground and sifted, furnish the *flour of mustard* used as a condiment.

The seed of white mustard yields an ash containing 25·78 per cent. potash, 0·33 soda, 19·10 lime, 5·90 magnesia, 0·39 ferric oxide, 2·19 sulphuric anhydride, 1·31 silica, 44·97 phosphoric anhydride, and a trace of chloride of sodium: 100 parts of the fresh seeds yielded 4·07, and 100 parts of the dried seeds 4·45 parts ash; 100 parts of the air-dried seeds were found to contain 8·50 parts moisture and 1·212 parts sulphur. (Way and Ogston, Jahresb. 1850, Table B, p. 660.)

MUSTARD, OILS OF. *a. Fixed Oils.* White mustard-seed yields by pressure about 36 per cent. of a yellow nearly inodorous oil, which has a specific gravity of 0·9145 at 15°, and is not solidified by cold. When saponified with soda, it yields glycerin and a soap which is perfectly soluble in water, and when decomposed by hydrochloric acid, yields a solid crystalline acid, called erucic acid (ii. 501), and an oily acid having nearly the composition of oleic acid.

Black mustard-seed yields 18 per cent. of an oil similar to the preceding, having a density of 0·917°, but solidifying at temperatures below 0°. According to Darby (Ann. Ch. Pharm. lxix. 1), it yields by saponification, stearic acid, erucic acid, and an oily acid.

β. Volatile Oil. When the flour of black mustard, after being freed by pressure from the fixed oil, is moistened with water, left to itself for several hours, and then distilled with water, it yields a very pungent volatile oil, having the properties and composition of sulphocyanate of allyl, $C^4H^5NS = \left.\begin{matrix}CN\\C^3H^5\end{matrix}\right\}S$. It is especially distinguished by its behaviour with ammonia, with which it immediately unites, forming crystalline thiosinnamine or sulphocyanate of allyl-ammonium, $H^3(C^3H^5)N.CNS$ (see Sulphocyanic Ethers).

This volatile oil does not pre-exist in the seed of black mustard, but is produced from myronic acid (p. 1073) contained in the seed, under the influence of water and a peculiar ferment called myrosin (p. 1075), likewise existing therein. Accordingly, it is not produced unless the mustard-flour is macerated with water for some time previous to distillation. Its formation is likewise prevented by drying the flour at a high temperature, or by heating it with alcohol or acids, as by these processes the myrosin is rendered inactive.

The quantity of volatile oil obtained from black mustard is but small, amounting to only 0·2 per cent. according to Boutron and Robiquet, 0·55 per cent. according to Aschoff, and 0·5 per cent. according to Wittstock.

White mustard does not yield any volatile oil, because it does not contain myronic acid.

MYCLOCLONE. Syn. with Cerebrote (i. 830).

MYCODERMA. A generic name of the fungi (also called *Torvulæ*), which, according to Pasteur and others, are essential to the processes of vinous and acetous fermentation. See Pasteur (Bull. Soc. Chim. de Paris, 1861, p. 94; Jahresb. 1861, p. 726; Compt. rend. lv. 28; Jahresb. 1862, p. 475); also the articles Fermentation, Vinegar, and Wine, in this Dictionary.

MYCOMELIC ACID. *Alloxenide* (Laurent), *Alloxanamide* (Gerhardt), $C^4H^4N^4O^2.\frac{1}{2}H^2O$. (Liebig and Wöhler, Ann. Ch. Pharm. xxvi. 304.)—When aqueous alloxan is heated gently with ammonia, it becomes yellow, and on cooling deposits a yellow transparent jelly of mycomelate of ammonium (see Alloxan, i. 137), from the hot aqueous solution of which salt sulphuric acid precipitates mycomelic acid. When freshly precipitated, it is transparent and gelatinous; but when washed and dried it is a loose yellow powder, which reddens litmus. It is scarcely soluble in cold water, more soluble in hot; insoluble in alcohol and ether; soluble in alkalis without forming crystallisable salts: its solution in potash is decomposed by boiling, with evolution of ammonia. It decomposes alkaline carbonates.

It is a monobasic acid. The only mycomelate known, beside the ammonium-salt, is the silver-salt, which is precipitated in yellow flakes when the ammonium-salt is added to nitrate of silver.

According to Liebig and Wöhler's analysis, the acid retains its ½ atom of water when dried at 100°. Gerhardt (*Traité*, i. 514) regards it as alloxanamide (alloxan + $2NH^3 - 2H^2O$); Laurent (Compt. rend. xxxv. 629), as alloxanide (alloxanic acid + $2NH^3 - 3H^2O$).

According to Hlasiwetz (Ann. Ch. Pharm. ciii. 211), mycomelic acid is formed when uric acid is heated with water to 180–190° in a closed vessel. F. T. C.

MYCOSE or **TREHALOSE.** $C^{12}H^{22}O^{11}$.—Wiggers in 1833 (Ann. Ch. Pharm. i. 173), observed in ergot of rye a peculiar kind of sugar, which was more exactly investigated in 1857 by Mitscherlich (*ibid.* cvi. 15), who designated it as mycose. Berthelot in the same year (Ann. Ch. Phys. [3] liii. 232, lv. 272, 291), obtained from trehala-manna, the produce of a species of *Echinops*, growing in the East, a sugar which he called trehalose, and at first regarded as different from mycose; but on further examination he was led to infer that the two are identical. (See *Gmelin's Handbook*, xv. 299–301.)

Mycose is obtained from ergot of rye by precipitating the aqueous extract of the fungus with basic acetate of lead, removing the lead from the filtrate by sulphydric acid, evaporating to a syrup, and leaving the liquid to crystallise. Trehalose is obtained from trehala-manna by exhaustion with boiling alcohol.

Mycose (trehalose) forms shining rhombic crystals, containing $C^{12}H^{22}O^{11}.2H^2O$, which melt when quickly heated to 109°; but if slowly heated give off their water even below 100°. It has a strongly saccharine taste, dissolves easily in *water* and in boiling *alcohol*, but is insoluble in *ether*. The aqueous solution is dextro-rotatory. For trehalose, Berthelot found $[\alpha] = +199°$ (for $C^{12}H^{22}O^{11}.2H^2O$); the specific rotatory power of mycose is, according to Mitscherlich, $[\alpha] = +192·5°$.

By several hours boiling with dilute *sulphuric acid*, it is converted into dextroglucose. With strong *nitric acid* it forms a detonating nitro-compound; heated with dilute nitric acid it yields oxalic acid. In contact with *yeast* it passes slowly and imperfectly into alcoholic fermentation. It is not altered by boiling with *alkalis*, and does not reduce cuprous oxide from alkaline *cupric solutions*. Heated with *acetic* or *butyric acid*, it yields saccharides, not distinguishable from those which are formed in like manner from dextro-glucose (ii. 854, 859).

MYELIN. A kind of kaolin, found at Rochlitz, of a yellowish or reddish colour, and containing, according to Kersten, 37·62 per cent. silver, 60·50 alumina, 0.82 magnesia, 0·63 manganic oxide, and a trace of ferric oxide.

The name myelin is also applied by Kirchow and Beneke (Ann. Ch. Pharm.

cxxii. 249) to a peculiar fatty substance obtained by evaporating the alcoholic extract of hard-boiled yolk of egg, brain-substance, crystalline lenses, and other animal tissues. This substance—which is especially characterised by shooting out into peculiar spiral threads, or loops, when immersed in water or in a solution of sugar—is found, according to Beneke, in some of the lower animals (*e.g.* in *Helix Pomatia*, p. 140), and likewise in plants, viz. in young chlorophyll, in some flower-stalks, in certain seeds, especially in peas, and always accompanied by cholesterin. (Jahresb. 1862, p. 507.)

MYRICA-TALLOW. *Myrtle-wax.*—A solid fat, obtained by pressing the berries of *Myrica cerifera* (or *M. cordifolia*, John) with water. It is pale-green, translucent, brittle, and friable in the cold; of splintery fracture, less extensible when warm than beeswax; has an aromatic taste and odour. Specific gravity 1·005 (Moore, Sill. Am. J. [2] xxxiii. 113). Melts at 47° to 49° (Moore). When purified by treatment with boiling water and cold alcohol, it melts at 47·5°, and contains 74·03 per cent. C, 12·07 H, and 13·70 O (Lewy, Ann. Ch. Phys. [3] xiii. 448). It contains a large quantity of palmitic and a small quantity of myristic acid, for the most part in the free state, but to a smaller extent combined with glycerin; no oleic nor any volatile acid. (Moore.)

It dissolves in 20 pts. of hot alcohol, a portion (palmitin, according to Moore) remaining, however, undissolved, and on cooling ⅘ separates out; the solution, formed with aid of heat, solidifies on cooling, and when perfectly cold is no longer precipitable by water. It is nearly insoluble in cold ether, but dissolves in 4 pts. of boiling ether, the solution, as it cools, depositing the greater part of the tallow without colour, and itself retaining a fine green colour. Cold oil of turpentine softens, and hot oil of turpentine dissolves $\frac{1}{17}$ pt. of it, the solution on cooling depositing white opaque granules. It likewise dissolves easily in fixed oils.

MYRICIN. (Brodie, Ann. Ch. Pharm. lxxi. 244).—The portion of beeswax which is insoluble in boiling alcohol. It is prepared by exhausting beeswax with boiling alcohol till the alcoholic liquid no longer gives a precipitate with acetate of lead. The myricin thus obtained melts at 64°, and has a faint waxy odour. It consists chiefly of palmitate of myricyl, $C^{46}H^{92}O^2 = C^{16}H^{31}(C^{30}H^{61})O^2$; and by dissolving it in ether, and leaving the solution to evaporate, the palmitate of myricyl is obtained in light plumose crystals, melting at 71·5° or 72°, and easily saponified by potash, especially in alcoholic solution, yielding palmitic acid and hydrate of myricyl. Crude myricin yields, by saponification, the same products, together with small quantities of another acid, and a neutral substance resembling hydrate of ceryl (i. 838). Crude myricin yields by dry distillation a number of fatty acids, of which palmitic acid forms the largest portion, together with solid and liquid hydrocarbons. (See MELENE, p. 868).

MYRICYL, HYDRATE OF. *Melissic alcohol*, *Melissin*, $C^{30}H^{62}O = \left.\begin{matrix}C^{30}H^{61}O\\H\end{matrix}\right\}O.$ (Brodie, Phil. Trans. 1848; Ann. Ch. Pharm. lxxi. 144.)—This compound, which is the highest known alcohol of the series, $C^nH^{2n+2}O$, is obtained by the action of melting potash upon myricin. On dissolving the product in water, precipitating the milky liquid, which contains the alcohol in suspension, with chloride of barium, exhausting the precipitate with ether, and leaving the solution to evaporate, hydrate of myricyl is deposited, and may be purified by crystallising it from ether, till it melts at 85°. A good mode of purification also is to exhaust the precipitate with boiling alcohol, and dissolve the substance which is deposited from the alcohol in rock-oil or rectified, coal-tar oil.

The mother-liquor then retains in solution a small quantity of another substance which melts at 72° and gives by analysis the same numbers as hydrate of myricyl. Brodie supposes it to be an alcohol of similar constitution. When treated with potash-lime it yields an acid containing $C^{19}H^{69}O^4$. (?)

Hydrate of myricyl is a crystalline substance having a silky lustre. It contains, according to Brodie's analysis, 82·02—82·77 per cent. C, and 13·97—14·25 H. (calc. 83·19 C, 14·15 H, and 3·66 O.)

When subjected to *dry distillation* it partly sublimes unaltered, and is partly resolved into water and a solid hydrocarbon (melene, p. 868). Heated with *potash-lime* it gives off hydrogen, and is converted into melissate of potassium:

$$C^{30}H^{62}O + KHO = C^{30}H^{59}KO^2 + H^4.$$

With strong *sulphuric acid* it forms acid sulphate of myricyl. Chlorine converts it into a resinous body (*chloromelal*), which gives by analysis numbers corresponding to the formula $C^{30}H^{45.5}Cl^{14.5}O$.

MYRISTIC ACID. $C^{14}H^{28}O^2 = \left.\begin{matrix}C^{14}H^{27}\\H\end{matrix}\right\}O.$ (Playfair, Phil. Mag. [3] xviii. 202; Ann. Ch. Pharm. xxxvii. 153.—Heintz, Pogg. Ann. lxxxvii. 267; xc. 137; xcii. 429 and 588.—*Summary of the Results*, J. pr. Chem. lxvi. 1.—Uricoechea, Ann.

Ch. Pharm. xc. 369.—Schlippe, *ibid.* cv. 1.—Oudemanns, J. pr. Chem. lxxxi. 356 and 367.—Gm. xvi. 209).

This acid was discovered by Playfair, and obtained pure by Heintz. It occurs, as myristin (myristate of glyceryl), in nutmeg-butter (Playfair), in otoba-wax (Uricoechea), in dika-bread (ii. 330), amounting to more than one-half of the fatty acids contained therein; also in small quantity, together with many other fatty acids, in cocoanut-oil (Gorgeu, Ann. Ch. Pharm. lxvi. 314), in common butter (Heintz); in croton-oil (Schlippe); and in combination with ethal, or an analogous body, in spermaceti (Heintz). According to Heintz and Scharling, it may be produced artificially by heating ethal with potash-lime; but its formation in this way is doubtless due to the presence of methal or myristic alcohol (p. 1072) in the ethal employed.

Preparation. α. From *Spermaceti.*—When the fatty acids obtained, together with ethal, by the saponification of spermaceti, as described under LAURIC ACID, (p. 474), are dissolved in alcohol, a mixture of palmitic and stearic acids crystallises on cooling, while a portion of both these, and the whole of the myristic and lauric acids, remain in solution. By fractional precipitation with acetate of magnesium (at last, in presence of excess of ammonia) the alcoholic solution is again divided into two parts, the stearic, palmitic, and a portion of the myristic acid being thrown down as magnesium-salts, while the lauric acid and the rest of the myristic acid remain in solution.

Treatment of the precipitated magnesium-salts.—The magnesia is separated from the fatty acids by boiling them with dilute hydrochloric acid; the melting-point of each portion of acid so obtained is determined; and those portions which melt nearly at the same temperature, and do not differ essentially in their mode of solidifying, are mixed together. When, now, the mixture of acids is repeatedly crystallised from alcohol, and the melting-point of the crystallising portion determined every time, several successive crops of crystals are obtained from each mixture. These are to be considered pure:—1. When their melting-point remains the same after repeated crystallisation; 2. When they solidify, on cooling, in crystalline scales; and 3. When, on fractional precipitation of their alcoholic solutions with acetate of magnesium, portions having one and the same melting-point are obtained. The several portions of the same acid show also, when pure, the same melting-point after being mixed together as when separate. Sometimes, especially in the preparation of myristic acid, it is necessary to subject the single crystallisations anew to fractional precipitation, and to repeat the above treatment and examination of the magnesium-salts thus obtained. (Heintz, Pogg. Ann. xcii. 429.)

In this way Heintz obtained, by the first precipitation with acetate of magnesium, nineteen magnesium-salts, from each of which he separated the acids. He mixed together the *first six portions of acid*, the melting-points of which varied from 42·7° to 45°, allowed them to separate from alcohol, and repeated the crystallisation fourteen times: but even the last crystallisation proved to be a mixture of palmitic and stearic acids, and in no case was a pure acid obtained. By precipitating the mother-liquor from the first nine crystallisations in seven portions with acetate of magnesium, he succeeded in obtaining, from the first, second, and third portions, after eight or nine times repeated crystallisation, pure, or nearly pure, palmitic acid. The fourth and fifth portions, yielded by seven times repeated, the sixth and seventh by three times repeated crystallisation, myristic acid melting at 53·7, which showed the above signs of purity. Of the remaining acids of the nineteen magnesium-salts, the *seventh* and *eighth portions* did not yield a pure acid by repeated crystallisation, but were recognised as mixtures of palmitic and myristic acids. The 9—17*th portions* were mixed together. The part which first separated from an alcoholic solution did not yield a pure acid on repeated crystallisation; after returning it to the mother-liquor, therefore, a portion of the acids present was precipitated by the addition of a little acetate of barium. The filtrate mixed with water deposited, in the cold, crystals melting at 53·8°, which yielded, on recrystallisation, pure myristic acid. The acid separated from the *eighteenth* and *nineteenth portions*, proved, after three crystallisations, to be also myristic acid. The quantity of myristic acid obtained from spermaceti is but small.

β. From *common butter.*—The mixture of acids obtained by saponifying butter and decomposing the soap, is freed from volatile acids by boiling with water, and from oleic acid by treating the lead-salt with ether, afterwards dissolved in alcohol and allowed to crystallise. After removing by recrystallisation as much of the acid present as can be obtained with a melting-point of 56° or 57° (containing palmitic and stearic acids), the collected alcoholic mother-liquors are subjected to fractional precipitation with acetate of magnesium; the myristic acid is thrown down in the last portions of the precipitate, and may be obtained therefrom by recrystallisation, removing, if necessary, the substances at first precipitable by acetate of barium. (Heintz.)

γ. The acids obtained by the saponification of *dika-fat* yield myristic acid on repeated crystallisation from alcohol, while a second portion of the acid, together with lauric acid, remains in solution. This latter portion may be recovered by precipitating the solution in several parts with acetate of magnesium, separating the magnesia, and crystallising the separate portions of acid until the melting point rises to 53·8°. (Oudemanns.)

δ. From *Myristin*. Playfair saponifies the myristin of nutmeg-butter with strong caustic potash; washes the soap repeatedly with solution of common salt; and afterwards decomposes the hot aqueous solution with hydrochloric acid. The acid, which separates as a colourless oil, solidifying on cooling, when freed from all traces of hydrochloric acid by washing with water, yields, on repeated crystallisation from alcohol, Playfair's myristic acid, having a melting-point of 49·8° (impure, therefore, and contaminated with an acid containing a smaller proportion of carbon). (Heintz.)

ε. By saponifying *otoba fat*, acids are obtained, from an alcoholic solution of which acetate of magnesium precipitates only, or chiefly, myristic acid, while oleic acid remains in solution. (Uricoechea.)

Properties.—Myristic acid forms white, shining, crystalline laminæ, resembling palmitic acid. It has an acid reaction, is perfectly insoluble in *water*, but dissolves easily in hot *alcohol*, crystallising on cooling; it is perfectly insoluble in *ether*. It melts at 53·8°, and solidifies on cooling in crystalline scales. (Heintz.)

TABLE *of the Melting-points of Mixtures of Lauric and Myristic Acids, according to Heintz.*

A mixture of—		Melts at	Solidifies at	Mode of solidifying.
Myristic acid.	Lauric acid.			
90	10	51·8°	47·3°	Crystalline scales.
80	20	49·6	44·5	Very fine crystals, not distinguishable as either needles or scales.
70	30	43·7	39	Ditto ditto
60	40	43	39	Uncrystallised, with isolated lustrous spots.
50	50	37·4	35·7	Large crystalline laminæ.
40	60	36·7	33·5	Uncrystallised, with isolated lustrous spots.
30	70	35·1	32·3	Uncrystallised, wavy.
20	80	38·5	33	Ditto ditto
10	90	41·3	36	Crystalline needles.

It will be observed that when the lauric acid amounts to 40 per cent. or more, the melting-point of the mixture lies below that of either constituent. This is generally the case in mixtures of fatty acids, when the quantity of the more fusible constituent exceeds a certain portion of the whole.

Decompositions.—1. Myristic acid subjected to *dry distillation*, is partly decomposed and partly volatilised unaltered.—2. On boiling with *nitric acid*, a part is converted into soluble products, with evolution of red vapours, the remaining undissolved portion behaving like unchanged myristic acid (Playfair).—3. By the dry distillation of the calcium-salt, myristone is produced (Overbeck).—4. A mixture of myristate and formate of calcium yields a repulsive-smelling oil, which deposits a small quantity of a solid product. This last, purified by recrystallisation, forms small, white, crystalline scales containing a larger proportion of carbon and hydrogen than would be contained in myristic aldehyde (Limpricht, Ann. Ch. Pharm. xcvii. 371).—5. Myristate of potassium heated with *oxychloride of phosphorus*, yields myristic anhydride; with *chloride of benzoyl*, benzo-myristic anhydride. (Chiozza and Malerba.)

MYRISTATES.—Myristic acid is monobasic, the general formula of the myristates being $C^{14}H^{27}MO^2$ or $C^{28}H^{54}M''O^4$, according as they contain mono- or di-atomic metals. The myristates of the alkali-metals are not decomposed by water (like the stearates) with formation of acid salts. (Playfair.)

Myristate of Barium, $C^{28}H^{54}Bba''O^4$, is obtained from chloride of barium and myristate of potassium by double decomposition (Playfair). Heintz precipitates hot alcoholic myristic acid with a hot concentrated aqueous solution of acetate of barium, and washes the precipitate with weak alcohol and hot water. Oudemanns precipitates the ammonia acid with chloride of barium. It is a very light crystalline powder, consisting of thin microscopic nacreous laminæ. It is very slightly soluble in water and alcohol, and decomposes before melting.

Myristate of Copper, $C^{28}H^{54}Ccu''O^4$, is obtained by precipitation, as a very light, loose, bluish-green powder, consisting of microscopic needles. It becomes deeper-coloured when heated above 100°, and cakes together before melting.

Myristate of Lead, $C^{28}H^{54}Ppb''O^4$, obtained by precipitation, is a white, loose, amorphous powder which melts at 100°—120°, and solidifies on cooling, in a white, opaque, amorphous mass (Heintz). An *aceto-myristate of lead*, $C^4H^6Ppb''O^4.4C^{28}H^{54}Ppb''O^4$, is obtained as a heavy white powder, insoluble in water, by heating myristin for several days with basic acetate of lead.

Myristate of Magnesium. $C^{28}H^{54}Mmg''O^4$.—Myristic acid, to which ammonia and sal-ammoniac have been added, is precipitated by sulphate of magnesium, and the precipitate washed with water. Very light powder, consisting of microscopic needles; becoming transparent at 140°, semi-fluid at 150°, and decomposing at a higher temperature. The salt dried in the air contains 9·54 per cent. water (3 at. = 10·15 per cent. H^2O). (Heintz.)

Myristate of Potassium. $C^{14}H^{27}KO^2$.—Myristic acid is digested with concentrated aqueous carbonate of potassium; the product evaporated to dryness, and the myristate of potassium extracted by absolute alcohol. It forms a white crystalline soap, easily soluble in water and in alcohol, insoluble in ether. (Playfair.)

Myristate of Silver, $C^{14}H^{27}AgO^2$, is obtained by double decomposition, from the sodium-salt and nitrate of silver, as a white, light, amorphous powder, turning slightly grey when exposed to light. It decomposes above 100°, without melting (Heintz); dissolves in aqueous ammonia, and forms, by spontaneous evaporation, large transparent crystals. (Playfair.)

Myristate of Sodium, $C^{14}H^{27}NaO^2$.—A boiling aqueous solution of carbonate of sodium, quite free from sulphate and chloride, is added in excess to boiling alcoholic myristic acid, and the mixture is evaporated completely to dryness in the water-bath. The residue is then extracted with boiling absolute alcohol, and filtered boiling hot. The filtrate, which solidifies to a jelly on cooling, is liquefied by warming, and mixed with water in the proportion of one-eighth of the alcohol employed, whereby a mother-liquor is formed which takes up any foreign salts present. On again solidifying, the salt is collected on linen and strongly pressed. (Heintz.)

MYRISTIC ALCOHOL. *Methal.* $C^{14}H^{30}O = \left.\begin{matrix}C^{14}H^{29}\\H\end{matrix}\right\}O$.—This alcohol is supposed to exist together with cetylic alcohol or ethal, $C^{16}H^{34}O$, and others of the same series, in commercial spermaceti. When this substance is saponified, salts of stearic, palmitic, myristic, and lauric acids are obtained, together with crude ethal. Now when the latter is recrystallised from alcohol, pure ethal or cetylic alcohol (i. 841), crystallises whilst the homologous compounds, *stethal* $C^{38}H^{18}O$, *methal* $C^{14}H^{30}O$, and *lethal* $C^{12}H^{26}O$, remain in smaller quantity in the mother-liquors, inasmuch as the alcohols obtained from these mother-liquors (after the removal of the admixed fatty acids by repeated treatment with alcoholic potash and addition of water), yield, when heated with potash-lime to 275°—280°, as long as hydrogen continues to escape, stearic, palmitic, myristic, and lauric acids. (Heintz, Ann. Ch. Pharm. xcii. 299; xcvii. 271; J. pr. Chem. lxvi. 19.)

MYRISTIC ANHYDRIDE. $C^{28}H^{54}O^3 = (C^{14}H^{27}O)^2.O$. (Chiozza and Malerba, *Gerh. Traité*, ii. 789.)—Obtained, like other anhydrides of the same series, by the action of oxychloride of phosphorus on myristate of potassium. It is a fatty substance, which scarcely exhibits any crystalline texture. Its melting point is a few degress lower than that of myristic acid. When slightly heated, it gives off vapours having a disagreeable odour. It is but slowly saponified by boiling caustic potash.

MYRISTIC ETHERS. *a. Myristate of Ethyl*, $C^{14}H^{27}(C^2H^5)O^2$.—Dry hydrochloric acid gas is passed into a hot solution of myristic acid in absolute alcohol, and the oil which separates on cooling is washed repeatedly with cold, and afterwards dissolved in a small quantity of warm alcohol. The layer of oil again formed on cooling, after being separated from the alcohol and cooled, deposits large, hard, very easily fusible crystals, from which the mother-liquor is to be decanted (Heintz). The specific gravity of myristic ether is 0·864 (Playfair). It dissolves easily in hot alcohol and in ether.

β. Myristate of Glyceryl. Myricin. $C^{45}H^{86}O^6 = \left.\begin{matrix}(C^3H^5)'''\\(C^{14}H^{27}O)^3\end{matrix}\right\}O^3$. (Playfair, *loc. cit.*)—When nutmegs, after exposure to the vapour of boiling water, are pressed between hot iron plates, a fatty matter called nutmeg-butter is separated, consisting of an oily liquid, which has not been examined, and a solid crystallisable fat, which is myristin. To separate the latter, the crude fat is digested with alcohol of ordinary strength; the myristin, which floats on the surface of the liquid, is dissolved in boiling ether; and the crystals which separate on cooling are pressed between bibulous paper, then redissolved, and submitted to alternate pressure and crystallisation till they melt constantly at 31°. (Playfair.)

Myristin thus prepared is crystalline, and has a silky lustre. It is soluble in all proportions in boiling ether, less soluble in boiling alcohol, insoluble in water. By dry distillation it yields acrolein and a fatty acid. Digested in the water-bath with a solution of basic acetate of lead, it yields insoluble myristate of lead and a solution ot glycerin.

Myristin contains, according to Playfair's analysis, 75·51—74·15 per cent. C, and 12·22—12·36 H, numbers agreeing nearly with the formula $C^{118}H^{226}O^{15}$ (calc. 74·51 C, 12·22 H, and 13·27 O), according to which myristin contains the elements of 4 at. myristic acid and 1 at. glycerin *minus* 7 at. water:

$$C^{118}H^{226}O^{15} = 8C^{14}H^{28}O^{2} + 2C^{3}H^{8}O^{3} - 7H^{2}O.$$

Such a constitution is, however, not very probable, no corresponding example of it being found among glycerides of well-known constitution. The above formula $C^{45}H^{86}O^{6}$, proposed by Weltzien, requiring 74·82 per cent. carbon and 11·91 hydrogen, agrees satisfactorily with the results of Playfair's analyses.

The fat or wax of the fruit of *Myristica officinalis*, and that of *M. sebifera*, possess properties similar to those of nutmeg-butter.

MYRISTICA. A genus of plants, including the nutmeg (*Myristica moschata*), the fruit and seeds of several species of which yield solid fats or waxes. *Bichuhyba-wax* is obtained from *Myristica Bicuhyba; Ocaba-wax* from *M. Ocaba* or *M. sebifera, Otoba-wax*, or *Otobite*, from *M. Otoba* (see Wax). The seeds and arillus (mace) of *M. moschata* also yield volatile oils by distillation with water. (See Mace, p. 740; and Nutmeg.)

MYRISTICIN. The camphor or stearoptene of volatile oil of nutmeg. (See Nutmeg.)

MYRISTIN. See Myristic Ethers.

MYRISTO-BENZOIC ANHYDRIDE. *Myristate of Benzoyl* or *Benzoate of Myristyl.* $C^{21}H^{32}O^{3} = C^{14}H^{27}O.C^{7}H^{5}O.O.$ (Chiozza and Malerba, *loc. cit.*)—Produced by the action of chloride of benzoyl on myristate of potassium. Crystallises in laminæ having a silky lustre and agreeable odour. Melts at 38°; solidifies at 36°. Not very soluble in ether.

MYRISTONE. $C^{27}H^{54}O = C^{14}H^{27}O.C^{13}H^{27}$. (Overbeck, Pogg. Ann. lxxxvi. 591.)—A product obtained by distilling myristate of calcium by small portions and at a gradually increasing temperature. It is purified by repeated crystallisation from boiling alcohol, and decolorised if necessary by animal charcoal.

Myristone forms colourless nacreous scales, inodorous and tasteless; they become electrical by friction. It melts at 75°, and solidifies in a radiated mass on cooling. It gave by analysis 81·81 per cent. C, and 14·07—13·95 H, whence Overbeck deduces the formula $C^{25}H^{50}O$ (calc. 81·96 C, 13·65 H). Gerhardt suggested the formula above given (calc. 82·23 C, 13·7 H, 4·07 O), representing the compounds as the acetone of myristic acid.

MYRISTYL, HYDRIDE OF. $C^{14}H^{30} = C^{14}H^{29}.H.$—This alcoholic hydride, more properly called hydride of tetradecatyl, is contained, together with many other hydrides of the same series, in American petroleum. It boils between 236° and 240°. (See Petroleum and Tetradecatyl.)

MYRONIC ACID. $C^{10}H^{19}NS^{2}O^{10}$ (from μύρον, a sweet-smelling ointment).—An acid occurring in the form of a potassium-salt in the seed of black mustard, and giving rise, by its reaction with myrosin, to the production of the volatile oil of black mustard (sulphocyanate of allyl). It was discovered by Bussy (J. Pharm. xvi. 39); and its existence, which was afterwards called in question by Thielau (Vierteljahrsschr. pr. Pharm. vii. 161), has been fully confirmed by the experiments of Ludwig and Lange (Zeitschr. Chem. Pharm. 1860, pp. 430 and 577) and of Will and Körner (Ann. Ch. Pharm. cxxv. 257; Jahresb. 1863, p. 495). According to Winckler (Jahresb. 1849, p. 436), myronate of potassium likewise exists in horseradish.

Preparation of the Potassium-salt.—Two pounds of black mustard-seed pulverised but not freed from fixed oil by pressure, are boiled with 2½ to 3 pounds of alcohol of 80 to 85 per cent. in a glass flask placed in a water-bath till about half a pound of the alcohol has passed off; the powder is then pressed, and the residue is subjected to the same treatment. The press-cake (weighing from 660 to 670 grms.), after being well-dried and pulverised, is next macerated for about twelve hours with 3 pts. of cold water; the liquid is removed by decantation and pressure; the residue is again treated with 2 pts. water; the watery extracts are evaporated to a syrup, with addition of carbonate of barium (carbonate of lead would give rise to the formation of sulphide of lead); the syrup is boiled with 3 or 4 pounds of alcohol of 85 per cent.; and the undissolved residue is treated in the same manner with 2 pounds of alcohol. The united alcoholic extracts are filtered after standing for 24 hours; the alcohol is distilled off, and the clear residue left to crystallise in shallow dishes. Lastly, the crystalline mass which separates after a few days is stirred up to a thin pulp with alcohol of 75 per cent. then strongly pressed between linen cloths, and the nearly white cake thus obtained is repeatedly crystallised from alcohol of 84 to 90 per cent. Two pounds of mustard-seed thus treated yield, on the average, from 5 to 6 grms. of myronate of potassium. The portion remaining in the mother-liquors may be used for the preparation of cyanide of allyl (Will and Körner). This mode of preparation, and the similar method adopted by Ludwig and Lange, do not differ in any essential particular from that originally given by Bussy.

Myronic acid may be obtained from the potassium-salt, either by mixing the aqueous solutions of 100 pts. of this salt and 38 pts. tartaric acid, evaporating to a certain extent, and extracting the myronic acid with alcohol; or better, by converting the potassium-salt into a barium-salt, and precipitating its aqueous solution with an equivalent quantity of sulphuric acid. The colourless aqueous acid thus obtained leaves on evaporation an inodorous, bitter and sour, uncrystallisable syrup, which reddens litmus strongly, dissolves in *alcohol*, but is not perceptibly soluble in *ether*. It decomposes when more strongly heated, yielding various volatile products. Its dilute solution, when boiled for some time, gives off sulphydric acid. With an aqueous solution of *myrosin* it yields sulphocyanate of allyl. (Bussy.)

The **myronates** are inodorous and likewise yield sulphocyanate of allyl with aqueous myrosin. They are all, even the barium-, lead-, and silver-salts, soluble in water. The ammonium-, barium-, potassium- and sodium-salts are crystallisable. (Bussy.)

Myronate of Barium, $C^{10}H^{18}BaNS^2O^{10}$, obtained by decomposing the solution of the potassium-salt with tartaric acid and absolute alcohol, and digesting the resulting aqueous myronic acid with carbonate of barium, crystallises in easily soluble plates which become opaque and milk-white on exposure to the air, and are decomposed by heat, giving off oil of mustard and leaving sulphate of barium. (Will and Körner.)

Myronate of Potassium, $C^{10}H^{18}KNS^2O^{10}$, crystallises from alcohol in silky needles grouped like crystals of wavellite; from water, in short, transparent glassy prisms of rhombic character. It has a cooling bitter taste, dissolves very easily in water, with difficulty in dilute alcohol, is nearly insoluble in absolute alcohol, and quite insoluble in ether, benzene, and chloroform. The solutions are neutral and do not act on polarised light. The salt is anhydrous and contains the elements of oil of mustard, glucose and acid sulphate of potassium, into which products it is easily decomposed:

$$C^{10}H^{18}KNS^2O^{10} = C^4H^5NS + C^6H^{12}O^6 + KHSO^4.$$

The dilute aqueous solution mixed with *myrosin*, or with a recently prepared aqueous extract of white mustard, becomes turbid in a short time, acquiring an acid reaction, and giving off the odour of oil of mustard. The solution then contains sulphuric acid and dextroglucose; the turbidity arises from free sulphur mixed with an insoluble organic substance probably formed from the myrosin (Will and Körner). Somewhat similar results of the decomposition of myronate of potassium have been obtained by Ludwig and Lange, who however assign to it the improbable formula $C^{20}H^{19}KNS^4O^{19}$. Myronate of potassium is not decomposed by emulsin, or an extract of sweet almonds, or by yeast or saliva.

When myronate of potassium is heated to boiling with a small quantity of *baryta-water*, a precipitate of barytic sulphate is formed, with copious evolution of mustard-oil. The same precipitate, containing half the sulphur in the original salt, is likewise formed when the solution of the potassium-salt previously made alkaline is precipitated by baryta-water in the cold; but in this case, the other elements of the mustard-oil remain in the solution in the form of a compound precipitable by lead-salts, and easily separable into mustard-oil and glucose.

Potash-ley of specific gravity 1·28, mixed with dry myronate of potassium, becomes spontaneously heated to the boiling point, giving off the odour of mustard-oil, cyanide of allyl, and ammonium.

Myronate of potassium, treated with *zinc* and *hydrochloric acid*, continually gives off sulphydric acid, which is likewise evolved, though more slowly, by boiling with hydrochloric acid alone. The solution then contains glucose, an ammonium-salt, and half the sulphur in the form of sulphuric acid.

A solution of myronate of potassium, mixed with *neutral acetate of lead*, yields a yellowish-white precipitate, easily soluble in acetic acid, and apparently containing all the elements of myronic acid. *Mercurous nitrate* forms a yellowish-white precipitate, which is decomposed by heat, with formation of mustard-oil.

When a moderately concentrated aqueous solution of myronate of potassium is mixed with *nitrate of silver*, nitric acid is set free, and a white curdy precipitate is formed, containing, when dried over oil of vitriol, the elements of sulphocyanate of allyl and sulphate of silver ($C^4H^5Ag^2NS^2O^4 = C^4H^5NS.Ag^2SO^4$). Its formation is represented by the equation,

$$C^{10}H^{18}KNS^2O^{10} + 2AgNO^3 = C^4H^5Ag^2NS^2O^4 + C^6H^{12}O^6 + KNO^3 + HNO^3.$$

This silver-compound, heated either alone or with water, is resolved into sulphocyanate of allyl, sulphate of silver and sulphide of silver; it is also decomposed, with evolution of mustard-oil, by *chloride* or *sulphide of barium*, or by *zinc*. When it is treated with *hydrochloric acid*, the liquid filtered from the chloride of silver contains half the sulphur in the form of sulphuric acid, but no sulphydric acid or sulphocyanate of allyl is produced. The silver-compound, suspended in a large quantity of water, is decomposed by *sulphydric acid*, with formation of a precipitate of sulphur and sulphide of silver; and the strongly acid filtrate, which contains half the original quantity of sulphur in the form of sulphuric acid, yields by repeated distillation an oily layer, consisting of cyanide of allyl, $C^3H^5.CN$:

$$C^4H^5Ag^2NS^2O^4 + H^2S = C^4H^5N + Ag^2S + S + H^2SO^4.$$

The cyanide of allyl thus produced differs considerably in its properties from that which Lieke obtained by the action of cyanide of silver on iodide of allyl (ii. 203). It is a colourless neutral oil of agreeably alliaceous odour and burning aromatic taste. Specific gravity = 0·8389 at 12·8°. Vapour-density = 2·32 (calc. 2·31); boiling point 116° (corrected 118·3°). Heated with strong potash-ley in a sealed tube, it is resolved into ammonia and crotonic acid, $C^4H^6O^2$. (Will and Körner.)

MYROSIN. An emulsion-like substance, of the albuminous or protein class, contained in the seeds of black and white mustard, and possessing the property of decomposing the myronate of potassium contained in the former, with production of sulphocyanate of allyl or volatile oil of mustard. It is likewise contained in the seeds of other cruciferous plants, viz. *Raphanus sativus*, *Brassica Napus*, *Br. oleracea* and *Br. campestris*, *Alliaria officinalis*, *Cheiranthus Cheiri*, *Draba verna*, *Cardamine pratensis*, *C. amara* and *Thlaspi arvense*. (Lepage.)

To prepare it, pulverised white mustard is exhausted with cold water; the filtrate evaporated to a syrup at a temperature below 40°; the syrup precipitated by a moderate quantity of alcohol; the precipitate dissolved in water after the alcohol has been poured off; and the solution evaporated to dryness at a temperature below 40°.

Myrosin, as thus obtained, resembles other protein-compounds. When incinerated, it leaves sulphate of calcium.

In the state of aqueous solution, it is coagulated by heat and also by alcohol, and loses its power of eliminating oil of mustard from myronic acid, but recovers this power after immersion in water for twenty-four to thirty-six hours. It does not eliminate hydrocyanic acid from amygdalin.

The aqueous solution of myrosin is transparent, colourless, and gummy, and froths when agitated. (Bussy, J. Pharm. xxvi. 44; Winckler, Jahrb. pr. Pharm. iii. 93.)

MYROXOCARPIN. (Stenhouse, Ann. Ch. Pharm. lxxviii. 306.)—A crystallisable substance extracted from white Peru balsam (i. 496). On digesting this balsam with alcohol of ordinary strength, a great part dissolves, and the solution gradually deposits large crystals of myroxocarpin mixed with resin; they may be purified by recrystallisation with aid of animal charcoal.

Myroxocarpin crystallises in large thin, colourless, shining prisms, often an inch long. According to a determination by Miller, they belong to the trimetric system, the ratio of the principal axis, macrodiagonal and brachydiagonal, for the primary octahedron P, being as 1 : 0·9363 : 0·7553. Observed combination $\infty P . oP . \infty\breve{P}\infty . \breve{P}\infty . 2\breve{P}\infty . \bar{P}\infty . 2\bar{P}\infty$. Angle $\infty P : \infty P = 102° 12'$; $\bar{P}\infty : oP = 127° 4'$; $2\bar{P}\infty : oP = 110° 41'$; $\breve{P}\infty : oP = 133° 7'$; $2\breve{P}\infty : oP = 115° 5'$. The crystals are hard and brittle, insoluble in water, very soluble in hot alcohol and ether, tasteless, and neutral to test-papers. They give by analysis 77·18 per cent. carbon, and 9·5 hydrogen, which may be represented by the formula $C^{48}H^{35}O^{6}$, or $C^{48}H^{70}O^{6}$.

Myroxocarpin melts at 115° to a transparent glass, which does not crystallise on cooling, but if redissolved in boiling alcohol, is again deposited in the crystalline form. Heated considerably above its melting point, it yields a sublimate, together with much acetic acid, and an uncrystallisable resin.

It does not unite with *acids*, or with *alkalis* and is not attacked by boiling *potash-ley*.

Hot *nitric acid* slowly converts it into oxalic acid and an uncrystallisable resin. *Chlorine*, with aid of heat, likewise converts it into an amorphous resin.

MYROXYLIC ACID. The name given by Plantamour to a product of the decomposition of cinnameïn (i. 981) by alcoholic potash; probably impure benzoic acid.

MYROXYLON PEREIRAE. The tree which yields Peru balsam. From the bark of this tree there exudes a gum-resin, which, according to Attfield (Pharm. J. Trans. [2] v. 248), contains 77·4 per cent. resin, 17·1 gum (like gum-arabic), 1·5 woody fibre, and 4 water, together with volatile oil. It is uncrystallisable, and its alcoholic solution reddens litmus slightly. This gum-resin is therefore altogether of different nature from the balsam obtained from the fruit of the same tree (i. 496).

MYRRH. A gum-resin which exudes from *Balsamodendron Myrrha*, a terebinthaceous shrub growing in Arabia and Abyssinia. It occurs in large heavy tears of various size, reddish colour, and irregular shape, having an appearance of efflorescence on the surface, semi-transparent, fragile, shining with a greasy lustre on the fractured surface. It has a rough bitter taste, and a strong, very peculiar aromatic odour.

The following are analyses of myrrh:

Resin	23·0	27·8		44·76
Essential oil . . .	2·5	2·6		2·18
Gum	46·0	54·4		40·82
Mucilage				
Foreign matters (potassium-salts of sulphuric, benzoic, malic, acetic acid), &c.		1·4	(foreign matter and ash)	7·51
Water and impurities . . .		1·6		1·45

An alcoholic solution of myrrh concentrated by distillation, deposits as it cools a soft resin, like turpentine, soluble in ether, slightly soluble in caustic potash, and imparting a violet-red colour to nitric and acetic acid.

Another resin, called myrrhin, remains dissolved in the alcohol, and may be obtained by evaporation. It has the odour of myrrh, melts between 90° and 95°, and is soluble in ether. Heated for some hours to 168°, it swells up and gives off acid vapours (acetic or formic acid?), and leaves a red-brown transparent shining mass, without taste or smell, soluble in alcohol and ether, insoluble in cold and very slightly soluble in boiling potash. This product imparts a violet colour to cold nitric acid, and dissolves in sulphuric acid with red-brown colour. It gave by analysis 74·78 per cent. carbon, 8·06 hydrogen, and 17·16 oxygen. (Ruikholdt.)

The essential oil (myrrhol) obtained by distilling the alcoholic extract of myrrh with water, is thick, yellowish, has a rough taste and pungent odour. It thickens and turns brown in contact with the air, dissolves in alcohol and ether, and is precipitated by water from its alcoholic solution in the form of a yellowish milk, acid to test-paper. It contains, according to Ruikholdt, 79·61 per cent. carbon, 10·43 hydrogen, and 9·96 oxygen.

Gladstone (Chem. Soc. J. xvii. 11) has examined the volatile oil obtained by directly distilling myrrh with water. It was very viscid and of a brownish-green colour; and began to boil at about 266°, giving an oxidised oil, which quickly resinised and retained its greenish colour, and strong smell of myrrh, after repeated rectification. Specific gravity = 1·0189 at 15·5°. Index of refraction at 7·5 for the line A, 1·5196; D, 1·5278; H, 1·5472. Rotatory power = − 136.

MYRRHIN and **MYRRHOL.** See the last article.

MYRTLE. *Myrtus communis.*—The berries of this plant contain, according to Riegel (Pharm. Centr. 1850, p. 319), chlorophyll, a green soft resin, a volatile oil (occurring also in the leaves), a fixed oil, tannin, sugar, citric acid, malic acid, mucus, humous substances, and small quantities of potash and lime.

Of a specimen of the volatile oil of myrtle, examined by Gladstone (*loc. cit.*), three-fourths distilled over between 160° and 176°, leaving a reddish-brown residue which evolved sulphydric acid. The rectified distillate smelt like oil of bay, and exhibited the composition of a hydrocarbon isomeric with oil of turpentine, $C^{10}H^{16}$. Specific gravity = 0·8911 at 15·5°. Index of refraction at 14°, for the line A, 1·4623; for D, 1·4680; for H, 1·4879. Specific rotatory power = + 21°.

MYSORIN. Anhydrous cupric ortho-carbonate, found in Mysore (see CARBONATES, i. 783).

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TO

THE THIRD VOLUME.

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